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ERRATA

Page 228, *authors of paper: for* Ruzikča *read* Růžička.
Page 492, *title of paper:* for 1-dithiocarboxy-3-methyl-5-phenyl-pyrazoline *read* 1-dithiocarboxy-3-methyl-5-phenyl-pyrazole.
Page 633, *line* 20: *for* $k = M\varkappa^{-1}k_{MF}$ *read* $k = \eta\varkappa^{-1}k_{MF}$.
Page 640, *reference* 120: J. Lustěnec, J. Krekule u. V. Pokorná, *Biol. Plant.* (*Praha*), 1960, **2**, 223.
Page 713, *caption to Fig.* 3: *for* Silver-Bromopyrogallol colour red system *read* Silver-Bromopyrogallol red colour system.
Page 824, *title of paper: for* Oxidation of cobalt^{III} with iron^{II} chloride in 2,2′-bipyridyl *read* Oxidation of cobalt^{II} with iron^{III} chloride in 2,2′-bipyridyl solutions.
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APPLICATIONS OF INFRARED SPECTROSCOPY—III*

THE SIMULTANEOUS DETERMINATION OF METHOXYL AND ETHOXYL GROUPS

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Summary—Quantitative vapour-phase infrared spectroscopy permits the simultaneous determination of methoxyl and ethoxyl groups as alkyl iodides or bromides: when the methoxyl/ethoxyl ratio exceeds 4 : 1, determinations are only possible as bromides. The reaction-time involved is 30 min. Results, correct to within ±1% for each alkoxyl group, can be obtained on the micro-scale. The presence of sulphur does not interfere.

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PART II[1] of this series described a spectroscopic investigation of some of the reaction variables of the Zeisel determination, and results were reported for micro alkoxyl determinations on reference compounds. These showed that the spectroscopic method of determining the liberated alkyl iodides not only gave results comparable in accuracy and reproducibility with those obtainable by the more conventional methods, but also distinguished in the same analysis between different alkoxyl groups. On unknown compounds, this selective information cannot be obtained directly if the conventional iodometric or gravimetric finishes are used.[2,3]

Gran[2] reviewed the techniques available for the simultaneous determination of methoxyl and ethoxyl groups; the majority require time-consuming modification or extension to the standard Zeisel method. Techniques based on Martin and Vertalier's[4] use of gas chromatography were later introduced[5,6] which, although not comparable in accuracy with the more conventional methods, offered possibilities for future development. More recent publications, however, have merely reverted to modifying[7] the Willstätter and Utzinger[8] technique or to describing modifications[9,10] of the combustion method.[11]

This paper describes how the quantitative infrared technique[1,12] can be extended, without modification or loss in accuracy, to the simultaneous determination of both methoxyl and ethoxyl groups. Results, correct to within ±1% for both groups, can be obtained on the microscale. The reaction-time is 30 min, and only one weighing of the sample is involved. The presence of excess sulphur (which continues to cause difficulty[13]) in any form or quantity does not interfere.

EXPERIMENTAL

Gas-cells

Descriptions of the gas-cells used, and data giving their useful concentration range and sensitivity have been given.[1,12,14]

* Part II—see ref. 1.

Spectrometer

The spectrometer used was a Hilger H800 double-beam instrument, which has the following advantages: (*a*) accommodation of gas-cells up to 56 cm long, (*b*) linear recording of percentage absorption, with an accuracy of $\pm 0{\cdot}5\%$. This fixes the limiting accuracy of the method, and obviates the necessity of weighing 2–5 mg samples to the nearest microgram. (By adjustment of tares, all weighings were made within the range of the 0–30 mg graticule scale of an aperiodic direct-reading balance having an accuracy of $\pm 10\ \mu$g.)

Spectrometer conditions

For the calibration curve to be of maximum accuracy, the standard operating conditions (slit-width, scan speed, electronic gain etc.) must be carefully selected initially and subsequently rigorously controlled during determinations. The gas-cell carrier must be rigidly fixed, or fitted with some simple

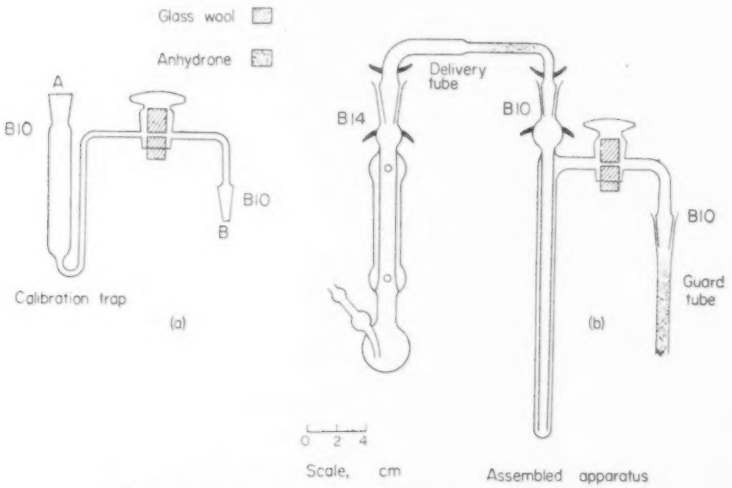

FIG. 1.—(*a*) Calibration trap. (*b*) Assembled apparatus.

locating device ensuring replacement each time in identical position with respect to the infrared beams.

Reproducibility of percentage absorption for a given concentration depends on the recorder zero-stability; any peak height must always be measured with respect to some arbitrarily fixed base-line or zero associated with the wave-length involved. All other conditions being constant, the base-line may be affected by small energy losses caused by fogged or scratched cell-windows, which must therefore be kept in good condition. Small local variations in base-line caused by such factors may, however, be satisfactorily compensated by adjustment of some auxiliary compensating device interposed in the reference beam.

Construction of calibration curves

Weigh the required amount of alkyl iodide in a micro weighing-bottle (12×4 mm) fitted with a leak-proof ground-glass stopper. Via *A*, place the bottle in the trap shown in Fig. 1(*a*), then immerse the limb of the trap in liquid nitrogen. Insert the requisite evacuated gas-cells at *A*, connect *B* to a suitable vacuum-line,[12] and evacuate the system with the trap still in coolant.

Vaporise the trapped alkyl iodide into the gas-cell, making the total pressure equal to atmospheric, by the technique already described.[13] Quantitative transfer, within the experimental limits of $\pm 1\%$, is easily achieved. Record the particular absorption peak selected for calibration (see below) six times, then calculate the mean peak height: this minimises any error in the peak heights drawn by the pen recorder, the reproducibility of which is $\pm 0{\cdot}25\%$.

Fundamentally, peak areas are proportional to concentration, but at the partial pressures used

peak heights are sensitive to concentration changes and are, under standard conditions, much easier to measure. "Pressure-broadening" effects do not cause complications.[12] Consequently, calibration curves can be constructed with reference to peak heights. Fig. 2 shows typical curves obtained.

Efficiency of trapping

Various weights of alkyl iodides were added to the reaction-flask and volatilised using flow-rates between 4 and 20 ml per min. At each flow-rate, recoveries ranged from 99·0–101·0% with an equal distribution of high and low results. In several experiments, two absorption traps were connected in series: in no case was alkyl iodide detectable in the second trap. These experiments led to ±1% being claimed as the accuracy of the method. In practice, results better than these limits can be expected (see Table I).

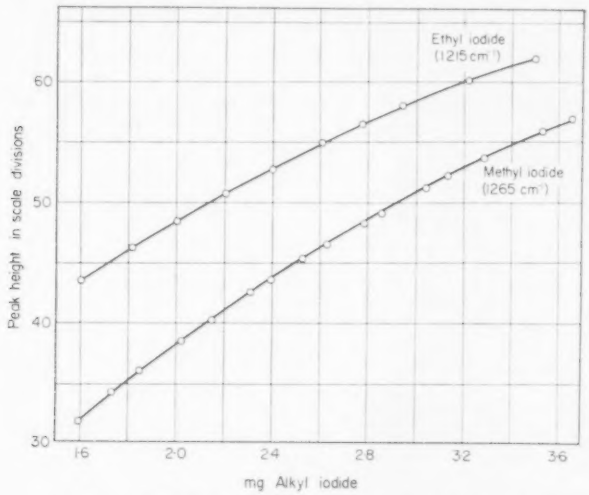

FIG. 2.—Calibration curves for methyl iodide and ethyl iodide.

Alkoxyl determinations

Details of the apparatus, reagents, flow-gas, heating, reaction-time, and weighing of samples have been described.[1] For volatile samples, the described technique obviating use of double distillation[1] is used; it may also be applied to non-volatile and solid samples. The following technique, however, has been successfully used for solids: weigh the sample in a long-handled weighing spoon.[1] Add 20–40 mg phenol to the spoon, and warm *gently* over a hot-plate to form a homogeneous melt at as low a temperature as possible. Place the spoon in a reaction-flask to which 6 ml of hydriodic acid had been added, pre-conditioned as described,[1] and cooled.

Procedure

Attach the delivery tube (Fig. 1(*b*)), packed with fresh Anhydrone, to a clean trap fitted with an Anhydrone guard-tube: immerse the trap in liquid nitrogen. (This order of assembly minimises collection of atmospheric water-vapour in the trap.) Attach the B14 cone of the delivery tube to the reaction condenser, so assembling the apparatus as shown in Fig. 1(*b*). Adjust the nitrogen flow-rate to 6–8 ml per min, and begin heating the reaction-flask.

After 30 min reflux, remove and stopper the trap, keeping it immersed in coolant. When convenient, volatilise the trapped reaction products into the appropriate gas-cell. Draw the spectrum of the products—this reveals immediately which iodides are present. Then re-draw 6 times (ensuring that the correct base-line is given) the characteristic peak on which calibration of each iodide is based. Refer the average peak height for each iodide to the appropriate calibration curve, and hence determine the weight of alkyl iodides liberated.

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RESULTS

Interferences

Since iodine, hydrogen sulphide and hydrogen iodide vapours do not interfere with the spectroscopic determination, conventional Zeisel scrubbers are not necessary. Phosphine, however, does interfere; preconditioning of the hydriodic acid as described[1] is required, and subsequent addition of hypophosphites to decolourise dark reaction mixtures should be avoided. The use of colourless hydriodic acid is not necessary for quantitative results. Since water vapour must be excluded in spectroscopic determinations, the reaction products are trapped after passage through Anhydrone[1].

Choice of calibration peaks

Fig. 3 diagramatically represents the spectra given in the 800–1500 cm^{-1} region,

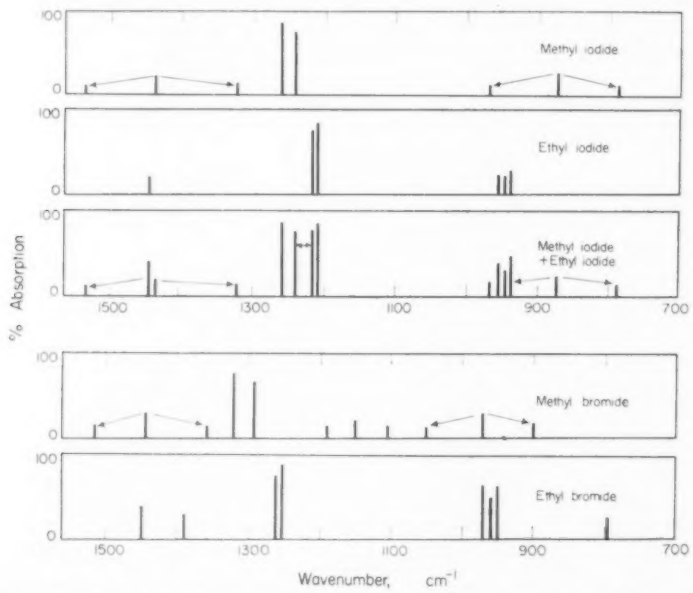

FIG. 3.—Representation of spectra given by methyl iodide, ethyl iodide, methyl bromide and ethyl bromide.

at a scan speed of 127 cm^{-1} per min, by methyl iodide, ethyl iodide, and by a mixture of the two. If a vapour contains only one component, calibration can be based on any convenient absorption peak in the spectrum, although maximum sensitivity and accuracy will clearly be obtained if calibration is based on the most intense absorption. In mixtures, however, over-lapping or coincidence of peaks can occur. Calibration for a particular component must then be based on the most intense absorption which is not masked or reinforced by peaks given by the other components present.

In the composite spectrum (Fig. 3) given by a mixture of methyl + ethyl iodides, very slight overlapping of peaks occurs at the normal scanning speed, so that the 1244 cm^{-1} peak of methyl iodide fractionally increases the height of the 1215 cm^{-1} ethyl iodide peak. The 1265 cm^{-1} methyl iodide peak is not masked, and so calibrations based on it give correct methoxyl values as shown by the typical results given in Table I.

Calibrations based on the 1215 cm^{-1} ethyl iodide peak, however, lead in this circumstance to high ethoxyl values: the more minor peaks given by ethyl iodide at 1450 cm^{-1} and 950 cm^{-1} are also subject to overlapping with minor methyl iodide peaks and so cannot be used.

Fortunately, this positive ethoxyl error was found to be a linear function of the

TABLE I. SIMULTANEOUS METHOXYL/ETHOXYL DETERMINATIONS

Compound or mixture	Weight taken, *mg*	Wt. alkyl iodide found		Corr. wt. $\overline{EtI}$ found,* *mg*	Methoxyl		Ethoxyl	
		$\overline{MeI}$, *mg*	$\overline{EtI}$, *mg*		found, %	theory, %	found, %	theory, %
Vanillin	7·41	6·94			20·4	20·4		
Phenacetin	3·29		3·00	2·86			25·2	25·1
Vanillin	10·24	9·52			20·3	20·4		
Phenacetin	3·02		2·82	2·63			25·3	25·1
Vanillin	2·03	1·90			20·5	20·4		
Phenacetin	4·28		3·75	3·71			25·1	25·1
Anisic acid	9·43	8·72			20·2	20·4		
Cmpd X†	7·20		3·15	2·98			12·0	12·0
Cmpd Y†	2·60	6·26			52·7	52·3		
			2·40	2·28			25·8	25·3
Cmpd Z†	1·42	0·98			15·1	15·0		
			3·22	3·20			65·1	65·5

* Corrected weight $\overline{EtI}$ = (wt. $\overline{EtI}$ found) − (0·019)(wt. $\overline{MeI}$ found).

† Origin of samples:
Cmpd X: 4-chloro-2-ethoxy-p-tosyl-1-naphthylamine (Prof. F. Bell)
Cmpd Y: 1:1:3-trimethoxy-3-ethoxypropane
Cmpd Z: 1:1:3-triethoxy-3-methoxypropane
L. Light and Co. Ltd. (redistilled).

weight of methyl iodide present, and a correction factor (0·019), applicable to a particular set of standard spectrometer conditions, was calculable. When

$$(0{\cdot}019) \times (\text{weight of methyl iodide found})$$

was subtracted from the actual weight of ethyl iodide found, the results shown in Table I were obtained for methoxyl-ethoxyl compounds or for synthetic mixtures ranging in composition from methoxyl/ethoxyl = 3:1 to 1:3.

At low ethoxyl contents, the 1215 cm^{-1} ethyl iodide absorption occurs as a shoulder on the 1244 cm^{-1} methyl iodide peak and determinations become inaccurate: at methoxyl/ethoxyl ratios $> 4:1$, there is no measurable ethyl iodide peak height and the method fails. Although such combinations must be rare in actual chemical compounds, they could readily be met in determinations on mixtures of methoxyl and ethoxyl compounds. Such mixtures can be analysed by using hydrobromic acid in place of hydriodic acid during reflux.

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Alkoxyl determinations using hydrobromic acid

Constant-boiling hydrobromic acid (sp. gr. 1·47) is effective in cleaving alkoxyl groups: it produces alkyl bromides quantitatively from esters and ethers almost as quickly (15–20 min for methyl and ethyl) as hydriodic acid forms the corresponding iodides. Alkyl bromides are as conveniently estimated as alkyl iodides by the infrared technique if the required calibration curves are constructed (the manometric technique[12] must be used for methyl bromide, b.p. 3·6°). Moreover, Fig. 3 shows that the 1320 cm^{-1} absorption of methyl bromide is so widely separated from the 1250 cm^{-1} peak of ethyl bromide that calibrations based on each of these are valid for the analysis of all possible methoxyl/ethoxyl percentage compositions. The only slight disadvantage in the use of the bromides is a small decrease in sensitivity. Gas-cell "B"[14] permits determination of approximately 2–6 mg of alkyl bromide as opposed to 1–4 mg of alkyl iodide; this requires that sample weights of alkoxyl compounds must be approximately doubled when determination as the bromide is used. Results equal in accuracy to those shown in Table I are, however, obtainable without the necessity of using a correction factor.

CONCLUSIONS

The method described permits satisfactory simultaneous determinations of methoxyl and ethoxyl groups on the micro scale. Although Table I shows only a few typical results, many determinations have been made during the past 18 months on a wide range of polyfunctional compounds, each of which contained, in addition to alkoxyl, one or more of the following groups: —F, —Cl, —Br, —I, —NO, —NO_2, —NH_2, =NH, —N=N—, =S, —SO_3H, ≡PO_4, —PS, =Se. Satisfactory results were obtained on pure samples; in our experience, some organic compounds are surprisingly difficult to purify sufficiently for satisfactory results to be obtained in the alkoxyl determination, which is a rigorous functional group analysis.

The accuracy obtainable, small samples required, short reaction time, elimination of conventional scrubbers, and absence of interference from sulphur combine to make this spectroscopic method undoubtedly superior to any method previously described for simultaneous determination of alkoxyl groups. At the present time, when ever-increasing numbers of chemists have access to an infrared spectrometer, this method should be of general interest.

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Zusammenfassung—Quantitative Infrarotspectroskopie in der Gasphase erlaubt die gleichzeitige Bestimmung von Methoxyl- und Äthoxylgruppen als Alkalijodide oder Bromide. Wenn das Verhältnis Methoxyl:Äthoxyl den Betrag von 4:1 überschreitet kann die Bestimmung nur über die Bromide durchgeführt werden. Die benötigte Reaktionszeit ist 30 Minuten. Die Resultate, innhalb von ±1% genau, können für Proben im Mikrobereich erhalten werden. Gegenwart von Schwefel stört nicht.

Résumé—La spectroscopie infra-rouge quantitative en phase vapeur permet le dosage simultané des groupements méthoxy et éthoxy à l'état d'iodures ou de bromures d'alkyl: quand le rapport méthoxy/éthoxy dépasse 4/1, les dosages ne sont possibles que pour les bromures. Le temps de réaction nécessaire est de 30 minutes. Les résultats, corrects dans l'intervalle de ±1 pour cent pour chaque groupement alkoxyl, peuvent être obtenus à l'échelle microscopique. La présence de soufre ne gêne pas.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—II

A LEAST SQUARE METHOD APPLIED TO MULTICOMPONENT SYSTEMS

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Summary—It is shown how the calculation of colorant concentrations in complementary tri-stimulus colorimetry can be improved by the application of the least square method, rather than by simple averaging of sets of results. In this improvement a matrix approach is especially useful, and the required equations are developed. Comparison of results obtained by the two methods shows the superiority of the matrix approach.

THE first paper in this series[1] considered the application of complementary tri-stimulus colorimetry to the photometric analysis of binary and ternary mixtures of colorants. It has been shown that more reliable results can be obtained in this manner than with the classical approach to photometric analysis. For a binary mixture, instead of two wavelengths, three "ranges" are selected, each range containing an appropriate number (5–10) of wavelengths at which absorbance readings are taken. With the use of an averaging process, the sum of the absorbance readings in each of the three ranges (denoted by U, V and W) are used to calculate the complementary colour co-ordinates u, v and w, which are defined by the following general formula

$$r_i = \frac{\mathrm{R}_i}{\sum_{i=1}^{i=n} \mathrm{R}_i} \tag{1}$$

where r_i is the complementary colour co-ordinate (u, v and w for $i = 1$, 2 and 3 respectively) and R_i is the sum of the absorbance readings in the ith range (U, V and W for $i = 1$, 2 and 3 respectively). The weighting factors for each range are assumed to have a value of unity. The complementary colour co-ordinates of a pure colorant are concentration-independent parameters and are characteristic of the particular colorant. The optical concentration of the solution of a colorant, J, is given by the formula

$$\mathrm{J} \equiv \kappa \sum_{i=1}^{i=n} \mathrm{R}_i \tag{2}$$

where κ is a constant, the numerical value of which for the present purpose can be deliberately taken to have a value of unity.

The overall absorptivity (the analogue of the extinction coefficient of the classical approach), E, is related to the analytical concentration by the formula

$$\mathrm{J} = \mathrm{C} \times \mathrm{E} \times l \tag{3}$$

where C is the analytical concentration and l is the length of the light path through the solution.

Each colorant is represented by a discrete point in the complementary colour diagram (usually a u–v plot; however, if convenient, a u–w or v–w plot may be employed). Any mixture of two colorants will have complementary colour co-ordinates which define a point located on the straight line connecting the complementary colour points of the two pure colorants. (This will be true only provided that the Lambert-Beer law is valid for each of the colorants and that their absorbances in a mixture are additive.) This "system line" can be calibrated in mole fraction (or any other fraction) thus making possible direct reading of that parameter for a mixture.

A partially graphical approach was presented in the earlier paper for the calculation of the concentration of the components of a binary and also of a ternary mixture of colorants. Further, a purely algebraic approach was given to determine these concentrations, which is based on the following set of equations:

$$U_m = C_a \times u_a \times E_a + C_b \times u_b \times E_b \tag{4a}$$

$$V_m = C_a \times v_a \times E_a + C_b \times v_b \times E_b \tag{4b}$$

$$W_m = C_a \times w_a \times E_a + C_b \times w_b \times E_b \tag{4c}$$

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where the subscripts m, a and b refer, respectively, to the colour parameters of the mixture and of each of the two components. Since there are three equations in the set and only two unknowns, the system is over-determined. Hence, three sets of results are obtained from the three possible pairings of the equations. The results will, of course, be identical where no erratic influences are present, or in the possible, but improbable, case that errors compensate each other. The three results may simply be averaged arithmetically in order to obtain a better result. However, when an erratic influence predominates in only one range, one result may differ markedly from the other two, and hence may be discarded in taking the average. But this is not an exact mathematical procedure.

A more reliable result will be obtained by applying the method of least squares to obtain mathematically the "best fit". This can be accomplished by applying appropriately the matrix approach developed by Bauman.[2] The treatment will be given in detail for the analysis of a binary mixture. Any number of components could be present, but then the number of ranges would have to be increased; in practice the mathematical effort would be tedious, and it might be simpler to exclude some components by separations, masking, *etc.*

In a general treatment, the sum of the absorbance readings of a mixture in any range is given by the following formula

$$R_i = \sum_{j=1}^{j=u} r_{ij} \times E_j \times C_j \tag{5}$$

where R_i is the sum of the absorbance readings in the ith range and all components present up to and including the jth and where r_{ij} is the complementary colour co-ordinate in the ith range for the jth colorant and E_j is its overall absorptivity.

For simplicity, the product $r_{ij} \times E_j$ may be denoted by K. Then in matrix notation, the equation (5) takes the form

$$\mathbf{R} = \mathbf{KC} \tag{6}$$

where R, K and C are the matrices of the corresponding parameters. Cramer's rule

is applicable to the solution of equation (6) if the number of equations equals the number of unknowns, as has been shown previously.[1] In order to apply the least square method effectively, more equations than unknowns are needed, but then the number of rows will not equal the number of columns and the simple determinant approach is no longer applicable. This difficulty can be overcome, as has been demonstrated by Bauman.[2]

Let d_i denote the difference between the sum of absorbance readings in the range i actually obtained in the analysis and the "true" (*i.e.*, the theoretical) value. Then the following formula is valid:

$$d_i = \sum_{j=1}^{j=n} r_{ij} \times E_{jx} \times C_j - R_i \tag{7}$$

or in matrix notation

$$D = KC - R. \tag{8}$$

To find the best set of values for C_j by the method of least squares, the values of d_i must be squared and summed, and the first derivative with respect to C must be set equal to zero. In other words $\frac{\partial}{\partial c} \sum d_i^2 = 0$. For the equation in matrix notation, the procedure may be developed stepwise as follows.

$$\Sigma d_i^2 = D^*D = (C^*K^* - R^*)(KC - R) \tag{9}$$

where the asterisks denote the transpose of the particular matrix. By multiplying out, the following is obtained:

$$D^*D = C^*K^*KC - C^*K^*R - R^*KC - R^*R. \tag{10}$$

Differentiation of this equation leads to

$$\frac{\partial D^*D}{\partial C} = \frac{\partial C^*}{\partial C} K^*KC + C^*K^*K \frac{\partial C}{\partial C} - \frac{\partial C^*}{\partial C} K^*R - R^*K \frac{\partial C}{\partial C} \tag{11}$$

and since $\frac{\partial C^*}{\partial C} = \frac{\partial C}{\partial C} = 1$ it follows that

$$\frac{\partial D^*D}{\partial C} = K^*KC + C^*K^*K - K^*R - R^*K\,. \tag{12}$$

Since the first term in (12) equals the second, and the third equals the fourth, it follows that

$$\frac{\partial D^*D}{\partial C} = 2(K^*KC - K^*R). \tag{13}$$

Setting the derivative equal to zero leads to the formula

$$K^*KC = K^*R. \tag{14}$$

Then by introducing the substitutions

$$K' = K^*K \tag{15}$$

$$R' = K^*R \tag{16}$$

the final equation is obtained which represents the condition of "best fit":

$$R' = K'C. \tag{17}$$

A mixture containing any number of components can be treated in this manner provided that the number of ranges selected exceeds by at least one the number of components, that is, $i \geqslant j + 1$.

It should be realised that the graphical treatment considered in the earlier paper[1] is no longer applicable when more than three ranges are selected, since a multi-dimensional plot would be required.

For a binary system, the extent of the calculations necessary for the matrix approach compares favourably with that using the algebraic approach, and more reliable results are obtained.

In the following paragraphs the entire matrix approach is presented in stepwise fashion for a binary system, with the general formulae paralleled by their application to the following assumed numerical results. Colorant *a* and *b* are assumed to be present in 0·100*M* solutions and to have the following complementary colorimetric parameters:

$$E_a = 1{\cdot}000 \quad u_a = 0{\cdot}100 \quad v_a = 0{\cdot}200 \quad w_a = 0{\cdot}700$$
$$E_b = 2{\cdot}000 \quad u_b = 0{\cdot}400 \quad v_b = 0{\cdot}400 \quad w_a = 0{\cdot}200.$$

From these data and the application of equations (4a)–(4c), the "theoretical" values of the complementary colorimetric parameters can be calculated for a mixture which contains 10·00 ml of each of the 0·100*M* solutions of the pure colorants in 100 ml of final solution, namely

$$U_m = 9{\cdot}000 \quad V_m = 10{\cdot}000 \quad \text{and} \quad W_m = 11{\cdot}000.$$

In order to demonstrate the improvement achieved by application of the method of least squares, the assumption is made that some erratic influence is present that causes a deviation in the *u*-range such that U_m has the "experimental" value of 9·300 rather than the "true" value of 9·000. The values of C_a and C_b can then be calculated by the algebraic approach, by inserting the numerical data into the set of equations (4):

$$9{\cdot}3 = 0{\cdot}1C_a + 0{\cdot}8C_b \tag{18}$$
$$10{\cdot}0 = 0{\cdot}2C_a + 0{\cdot}8C_b \tag{19}$$
$$11{\cdot}0 = 0{\cdot}7C_a + 0{\cdot}4C_b. \tag{20}$$

The values obtained by solving the three possible pairs of these equations are given in Table I, columns A, B and C.

It will be seen that one set of values, thus obtained, differs markedly from the other two. Hence, a better result is obtained by discarding this set of values and averaging the remaining two, rather than by averaging all three sets. Both averages are recorded in Table I.

TABLE I.—COMPARISON OF VALUES OBTAINED BY APPLYING DIFFERENT METHODS
Erratic influences operative only in the *u*-range.

	A Equations (18)–(19)	B Equations (18)–(20)	C Equations (19)–(20)	$\frac{A + B + C}{3}$	$\frac{B + C}{2}$	Least square method	True value
C_a	7·00	9·77	10·00	8·92	9·88	9·84	10·00
C_b	10·75	10·40	10·00	10·38	10·20	10·23	10·00

Since the erratic influence was assumed to be present only in the *u*-range, two sets of values had to be incorrect and one correct. In a practical case, the influences will most probably be operative in each of the three ranges and to different degrees. Hence, the distribution of errors and their magnitude will be more complex than in this simple demonstration example. In practical cases, it is usually not possible to discard "safely" one set of values, and all three must be averaged. In such a case the method of least squares will always yield a superior value.

The procedure takes the following form:

$$\underset{\mathrm{R}}{\begin{vmatrix} \mathrm{U}_m \\ \mathrm{V}_m \\ \mathrm{W}_m \end{vmatrix}} = \underset{\mathrm{K}}{\begin{vmatrix} u_a\mathrm{E}_a & u_b\mathrm{E}_b \\ v_a\mathrm{E}_a & v_b\mathrm{E}_b \\ w_a\mathrm{E}_a & w_a\mathrm{E}_b \end{vmatrix}} \underset{\mathrm{C}}{\begin{vmatrix} \mathrm{C}_a \\ \mathrm{C}_b \end{vmatrix}} \qquad \begin{vmatrix} 9{\cdot}3 \\ 10{\cdot}0 \\ 11{\cdot}0 \end{vmatrix} = \begin{vmatrix} 0{\cdot}1 & 0{\cdot}8 \\ 0{\cdot}2 & 0{\cdot}8 \\ 0{\cdot}7 & 0{\cdot}4 \end{vmatrix} \begin{vmatrix} \mathrm{C}_a \\ \mathrm{C}_b \end{vmatrix} \tag{21}$$

$$\mathrm{K}' = \underset{\mathrm{K}^*}{\begin{vmatrix} u_a\mathrm{E}_a & v_a\mathrm{E}_a & w_a\mathrm{E}_a \\ u_b\mathrm{E}_b & v_b\mathrm{E}_b & w_b\mathrm{E}_b \end{vmatrix}} \underset{\mathrm{K}}{\begin{vmatrix} u_a\mathrm{E}_a & u_b\mathrm{E}_b \\ v_a\mathrm{E}_a & v_b\mathrm{E}_b \\ w_a\mathrm{E}_a & w_b\mathrm{E}_b \end{vmatrix}}$$

$$\mathrm{K}' = \begin{vmatrix} 0{\cdot}1 & 0{\cdot}2 & 0{\cdot}7 \\ 0{\cdot}8 & 0{\cdot}8 & 0{\cdot}2 \end{vmatrix} \begin{vmatrix} 0{\cdot}1 & 0{\cdot}8 \\ 0{\cdot}2 & 0{\cdot}8 \\ 0{\cdot}7 & 0{\cdot}7 \end{vmatrix} = \begin{vmatrix} 0{\cdot}54 & 0{\cdot}52 \\ 0{\cdot}52 & 1{\cdot}44 \end{vmatrix} \tag{22}$$

$$\mathrm{R}' = \underset{\mathrm{K}^*}{\begin{vmatrix} u_a\mathrm{E}_a & v_a\mathrm{E}_a & w_a\mathrm{E}_a \\ u_b\mathrm{E}_b & v_b\mathrm{E}_b & w_b\mathrm{E}_b \end{vmatrix}} \underset{\mathrm{R}}{\begin{vmatrix} \mathrm{U}_m \\ \mathrm{V}_m \\ \mathrm{W}_m \end{vmatrix}} \qquad \mathrm{R}' = \begin{vmatrix} 0{\cdot}1 & 0{\cdot}2 & 0{\cdot}7 \\ 0{\cdot}8 & 0{\cdot}8 & 0{\cdot}4 \end{vmatrix} \begin{vmatrix} 9{\cdot}3 \\ 10{\cdot}0 \\ 11{\cdot}0 \end{vmatrix} = \begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix} \tag{23}$$

$$\mathrm{C} = (\mathrm{K}')^{-1}\mathrm{R}' = \underbrace{\underbrace{\frac{1}{0{\cdot}54 \times 1{\cdot}44 - 0{\cdot}52 + 0{\cdot}52}}_{=\,0{\cdot}5072} \begin{vmatrix} 1{\cdot}44 & -0{\cdot}52 \\ -0{\cdot}52 & 0{\cdot}54 \end{vmatrix}}_{(\mathrm{K}')^{-1}} \underbrace{\begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix}}_{\mathrm{R}'}$$

$$= \underset{(\mathrm{K}')^{-1}}{\begin{vmatrix} \dfrac{1{\cdot}44}{0{\cdot}5072} & \dfrac{-0{\cdot}52}{0{\cdot}5702} \\ \dfrac{-0{\cdot}52}{0{\cdot}5702} & \dfrac{0{\cdot}54}{0{\cdot}5702} \end{vmatrix}} \underset{\mathrm{R}'}{\begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix}} = \begin{vmatrix} 2{\cdot}8391 & -1{\cdot}0252 \\ -1{\cdot}0252 & 1{\cdot}0647 \end{vmatrix} \begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix} = \begin{vmatrix} 9{\cdot}840 \\ 10{\cdot}226 \end{vmatrix} \tag{24}$$

which is finally

$$\mathrm{C} = \begin{vmatrix} \mathrm{C}_a \\ \mathrm{C}_b \end{vmatrix} = \begin{vmatrix} 9{\cdot}84 \\ 10{\cdot}23 \end{vmatrix}.$$

The final result obtained by this matrix approach is also presented in Table I. Inspection of this Table reveals that the results obtained by the matrix approach are far superior to the averages obtained by combination of the three sets of results obtained by the algebraic method. Indeed, the set of results by the least square method differs only slightly from the averages obtained in the algebraic method after rejecting the obviously erratic set of results.

The results of a further example in which the erratic influences are operative in all three ranges are presented in Table II. The "experimental" values are assumed to be $U_m = 9{\cdot}300$, $V_m = 9{\cdot}700$ and $W_m = 10{\cdot}700$ and the true values to be the same as in the first example.

TABLE II. COMPARISON OF VALUES OBTAINED BY APPLYING DIFFERENT METHODS
Erratic influences operative in all three ranges.

	A Equations (18)–(19)	B Equations (18)–(20)	C Equations (19)–(20)	$\frac{A \times B + C}{3}$	$\frac{B + C}{2}$	Least square method	True value
C_a	4·00	9·31	9·75	7·69	9·53	9·84	10·00
C_b	11·12	10·46	10·41	10·66	10·54	10·21	10·00

It will be seen from Table II that the results are "poor" when the algebraic approach is employed, especially when the most discordant set of results is retained in averaging. In contrast, the matrix approach is far less affected by the erratic influences. In this example, nearly the same result is obtained with the matrix approach as in the first one. This finding is explained when it is considered that the three parameters are close in numerical value, and that the assumed errors are equal in magnitude but opposite in sign.

The impressive improvement obtained by the matrix approach justifies the additional calculation involved. Further, when an analysis of a given system is effected repeatedly, some of the intermediate parameters of the matrix operations are independent of the concentrations and need only be calculated once. Thus, in the first illustrative sample the calculation can proceed through the inverse of K′, which is denoted in equation (24) by $(K')^{-1}$. Then only R′ need be calculated for a particular analysis according to equation (23). The combination of K′ and R′ by the last step of equation (24) then yields immediately the concentrations of the two colorants.

The matrix approach has also been applied to the ternary system described in the earlier paper[1], namely the EDTA complexes of copper, nickel and cobalt in a buffered aqueous solution. In one particular mixture, the actual concentrations of the three colorants were 10·00 ml of 0·1*M* Cu-EDTA, 5·00 ml of 0·1*M* Ni-EDTA and 5·00 ml of 0·1*M* Co-EDTA per 100 ml of the final buffered solution. By using the three ranges and the algebraic approach (which does not represent an over-determination for the three-component system), the values obtained from experiment were, respectively, 9·96, 5·28 and 4·69 ml of 0·1*M* metal-EDTA solutions per 100 ml of final solution.

To apply the matrix approach of the present paper, a fourth range was chosen; however, the wavelengths in it were selected from those in the other three ranges in

order not to introduce an unfair advantage for the matrix approach in comparing results. The results obtained were respectively, 10·15, 5·13, and 5·07.

Admittedly the matrix calculation for a three-component system is tedious, especially the calculation of the transpose $(K')^{-1}$. Of course, where the analysis is to be effected repeatedly, this matrix parameter is calculated only once, thus reducing the calculation effort in further analyses. The general scheme for the calculation of the transpose of a three-by-three matrix is described below in order to aid the reader who may be less familiar with these mathematical operations.

Let the matrix A represent the following

$$A = \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}$$

Then the transpose of A, namely A^{-1}, can be calculated by the following scheme

$$A^{-1} = \frac{1}{\det |A|} \times T = \frac{1}{\det |A|} \begin{vmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{vmatrix}$$

where T is the transpose of the matrix of co-factors, which is the adjoint of A (also called the adjugate matrix of A) and det |A| is the numerical value of the determinant A calculated in the usual way. The co-factors are calculated by applying determinant calculations to each of the two-by-two determinants separately in the following matrix

$$A^{-1} = \frac{1}{\det |A|} \begin{vmatrix} \begin{vmatrix} b_2 & c_2 \\ b_3 & c_3 \end{vmatrix} & - \begin{vmatrix} b_1 & c_1 \\ b_3 & c_3 \end{vmatrix} & \begin{vmatrix} b_1 & c_1 \\ b_2 & c_2 \end{vmatrix} \\ - \begin{vmatrix} a_2 & c_2 \\ a_3 & c_3 \end{vmatrix} & \begin{vmatrix} a_1 & c_1 \\ a_3 & c_3 \end{vmatrix} & - \begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix} \\ \begin{vmatrix} a_2 & b_2 \\ a_3 & b_3 \end{vmatrix} & - \begin{vmatrix} a_1 & b_1 \\ a_3 & b_3 \end{vmatrix} & \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} \end{vmatrix}$$

In the application of this scheme to the problems considered in the present paper, less calculation effort is involved than the mathematical impedimenta suggest, since the original matrix possesses considerable symmetry, and therefore several terms occur repeatedly and need only be calculated once.

Zusammenfassung—Es wird gezeigt, dass die Berechnung der Konzentrationen der Komponenten von Mehrstoffsystemen in der komplementären Tristimuluskolorimetre erheblich verbessert werden kann, wenn statt einfacher Mittelung der Resultate die Methode der kleinsten Quadrate angewendet wird. Zur Durchführung der Berechnungen hat sich der Gebrauch von Determinanten und Matritzen als günstig erwiesen und die nötigen Gleichungen sind abgeleitet. Vergleich der nach beiden Methoden erhaltenen Resultate zeigt die klare Überlegenheit der neuen Methode.

Résumé—L'auteur montre que le calcul des concentrations de colorants dans la colorimétrie trichrome peut être amélioré par l'application de la méthode des moindres carrés plutôt qu'en prenant simplement la moyenne des séries de résultats. Dans cette amélioration, une approximation par matrice est spécialement utilisée, et les équations nécessaires sont développées. La comparaison des résultats obtenus par les deux méthodes montre la supériorité de l'approximation par matrice.

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INVESTIGATIONS WITH IRIDIUM-192 OF SEPARATIONS OF PLATINUM AND RHODIUM FROM IRIDIUM—II

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Summary—^{192}Ir has been used as a tracer in a study of the separation of platinum and rhodium from iridium by the use of mercury^{I} chloride or mercury^{II} chloride and hypophosphorous acid as a selective precipitant.

It has been found that platinum may be separated satisfactorily from iridium by the use of either mercury^{I} chloride or the mercury^{II} salt and hypophosphorous acid. In the presence of bromide, rhodium may be conveniently separated from iridium by precipitation using a slurry of mercury^{I} chloride. Iridium may be precipitated quantitatively by the slurry if iodide is present.

A new rapid procedure for the separation of rhodium and iridium and subsequent determination of the two metals is proposed.

INTRODUCTION

IN 1934 Pierson[1] showed that platinum and palladium were precipitated from certain solutions by mercury^{I} chloride (calomel). More recently, Powell[2,3] has found that platinum, palladium and rhodium may be precipitated from solutions of their chlorides in dilute hydrochloric acid by the addition of mercury^{II} chloride and the subsequent addition of hypophosphorous acid and heating. The metals, precipitated in this manner, settle rapidly in a readily filtering form which yields the pure metal on ignition. The reaction is apparently due to reduction of mercury^{II} to mercury^{I} by the hypophosphorous acid, followed by the reduction of the platinum metals in solution by the mercury^{I}. Hypophosphorous acid, alone, produces no precipitate except in the case of palladium. The procedure forms a simple means of separating platinum, palladium and rhodium from iridium.

In the present study ^{192}Ir has been used as a tracer in investigations of the separation of platinum and rhodium from iridium by precipitation with calomel and also with mercury^{II} chloride and hypophosphorous acid. In addition, a new rapid procedure for the separation and determination of milligram quantities of rhodium and iridium has been developed.

Stock solutions of platinum metals and ^{192}Ir used in the work were similar to those employed in the research previously reported.[4]

OXIDATION POTENTIALS

Relevant oxidation potentials for ion-electron half-reactions of calomel and complexes of platinum, rhodium and iridium are shown in Table I. The values are those given by Latimer[5] and the conventions employed by that author have been followed.

The recorded potentials indicate that mercury^{I} chloride should serve as a precipitant for iridium metal. However, it must be remembered that oxidation potentials measure energy differences and bear no relation to reaction kinetics. Many reactions which are energetically possible are not observed because they proceed too slowly to

be followed. In addition, oxidation potential values refer only to equilibrium conditions and many reactions are encountered in which such conditions do not exist.

Reductants other than mercury^{I} chloride, *e.g.* copper powder, do not easily precipitate iridium, although oxidation potentials suggest that reduction to the metal should occur. The problem has been discussed by Tertipis and Beamish.[6]

TABLE I.—STANDARD OXIDATION POTENTIALS IN ACIDIC SOLUTION

Equation	E°_{298}, *V*
$Cl^- + \frac{1}{2}Hg_2Cl_2 \rightleftharpoons HgCl_2$ (sat. soln.) + e	−0·53
$Pt + 4Cl^- \rightleftharpoons PtCl_4^{2-} + 2e$	−0·73
$PtCl_4^{2-} + 2Cl^- \rightleftharpoons PtCl_6^{2-} + 2e$	−0·68
$Rh + 6Cl^- \rightleftharpoons RhCl_6^{3-} + 3e$	−0·44
$Ir + 6Cl^- \rightleftharpoons IrCl_6^{2-} + 4e$	−0·835

PRECIPITATION OF PLATINUM AND SEPARATION FROM IRIDIUM

Solutions containing milligram quantities of platinum and iridium labelled with ^{192}Ir were prepared in 50 ml of dil. hydrochloric acid. These were heated to boiling, and either (*a*) 5 ml of 3% (w/v) mercury^{II} chloride and 5 ml of 10% (v/v) hypophosphorous acid or (*b*) solid mercury^{I} chloride or (*c*) a slurry of mercury^{I} chloride were added. (The slurry of mercury^{I} chloride was prepared by the addition of dil. hydrochloric acid to a hot solution of mercury^{I} nitrate in dil. nitric acid; the precipitate of mercury^{I} chloride was washed by decantation with distilled water until free from acid and was used with a little water as a semi-fluid mixture).

TABLE II.—SEPARATION OF PLATINUM FROM IRIDIUM

Platinum taken, *mg*	Iridium taken, *mg*	Conditions of separation	Platinum found, *mg*	Iridium found radiometrically in recovered platinum, *mg*
10·0	10·0	10% HCl,$HgCl_2$ + H_3PO_2	10·33	0·004
10·0	10·0	10% HCl,Hg_2Cl_2 (solid)	9·94	0·052
10·0	10·0	10% HCl,Hg_2Cl_2 (slurry)	10·10	0·005

In each case the resulting solution was boiled for 10 min and the precipitate of platinum was collected on a 9-cm Whatman No. 44 filter paper. The beaker was rinsed with hot 2% hydrochloric acid. Any precipitate adhering to the walls of the beaker was removed with a small piece of filter paper, which was then placed in a porcelain crucible together with the main precipitate and ignited in the usual manner.[7] The recovered platinum was mounted on a tared aluminium counting tray, weighed, and counted with a γ-scintillation counter, type 1186A.

In each test an aliquot of the labelled iridium solution was employed for a standard, as in the studies previously described.[4]

Results of these experiments are shown in Table II. In each case a satisfactory separation of platinum from iridium was obtained.

PRECIPITATION OF RHODIUM AND SEPARATION FROM IRIDIUM

Standard solutions of rhodium with labelled iridium in dilute hydrochloric acid were treated in a similar manner to the mixtures of platinum and iridium, except that the final samples of rhodium were reduced in hydrogen before weighing and counting.

It was found that when mercury^{II} chloride and hypophosphorous acid were used as the reducing agent, the weight of rhodium precipitated decreased with an increase

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in the hydrochloric acid concentration (Table III, tests 1–3). The contamination of the precipitate with iridium also decreased with an increase in the acid concentration.

In addition, it was found that either solid calomel or the freshly prepared slurry failed to precipitate rhodium quantitatively, even after re-treatment of the filtrate (Table III, tests 4–6).

TABLE III.—SEPARATION OF RHODIUM FROM IRIDIUM

Test	Rhodium taken, *mg*	Iridium taken, *mg*	Conditions of separation	Rhodium found, *mg*	Iridium found radiometrically in recovered rhodium, *mg*
1	10·0	10·0	2% $HCl,HgCl_2 + H_3PO_2$	10·14	0·082
2	10·0	10·0	10% $HCl,HgCl_2 + H_3PO_2$	9·85	0·076
3	10·0	10·0	20% $HCl,HgCl_2 + H_3PO_2$	9·76	0·050
4	10·0	10·0	10% HCl,Hg_2Cl_2 (solid)	2·74	0·016
5	10·0	10·0	10% HCl,Hg_2Cl_2 (slurry)	6·40	0·019
			Re-treatment of filtrate from test 5	2·46	0·164
6	10·0	10·0	10% HCl,Hg_2Cl_2 (slurry)	4·30	0·062

Precipitation of rhodium using calomel in the presence of bromide

The limited information available on oxidation potentials characteristic of the platinum metals[5] indicates that, in some cases, bromide complexes may be reduced more readily than the corresponding chloride complexes. It was decided, therefore, to investigate the effect of bromide on the reduction of rhodium by calomel. Separations were carried out as before, with an excess of mercury[I] chloride slurry and varying concentrations of hydrochloric acid and of potassium bromide.

Results shown in Table IV indicate that the presence of bromide led to a better recovery of rhodium. An increase in bromide concentration gave rise to a greater contamination of the rhodium with iridium, but the contamination could be reduced to a more acceptable level by increasing the acid concentration.

Further experiments were carried out involving a double precipitation of the rhodium. The rhodium from the first precipitation was collected on a 9-cm Whatman No. 44 filter paper, washed with 2% hydrochloric acid and redissolved from the paper with hot hydrochloric acid saturated with bromine. The solution was collected in the original beaker, evaporated to *ca.* 1 ml and diluted to 50 ml with 10% (v/v) hydrochloric acid. Five g of potassium bromide were added and the rhodium was re-precipitated with mercury[I] chloride slurry. Quantitative recoveries of rhodium were obtained in this manner and the contamination by iridium was negligible (Table IV, tests 10–12).

PRECIPITATION OF IRIDIUM BY CALOMEL IN THE PRESENCE OF IODIDE

It was found that iridium could be precipitated from the filtrates in the studies summarised in Table IV by the addition of 5 g of potassium iodide and a further quantity of mercury[I] chloride slurry. In many cases the recovery of the metal was not quantitative, and further tests were carried out to determine the most favourable conditions for complete precipitation.

The tests were made using different concentrations of hydrochloric acid, bromide and iodide, and various volumes of solution. It was found that less iridium was

TABLE IV.—SEPARATION OF RHODIUM FROM IRIDIUM USING A SLURRY OF CALOMEL IN THE PRESENCE OF BROMIDE

Test	Rhodium taken, *mg*	Iridium taken, *mg*	Conditions of separation using mercury[I] chloride slurry	Rhodium found, *mg*	Iridium found radiometrically in recovered rhodium, *mg*
1	10·0	10·0	50 ml 2% HCl + 1 g KBr	9·96	0·137
2	10·0	10·0	50 ml 10% HCl + 1 g KBr	9·82	0·097
3	10·0	10·0	50 ml 20% HCl + 1 g KBr	9·72	0·048
4	10·0	10·0	50 ml 2% HCl + 2·5 g KBr	10·58	0·749
5	10·0	10·0	50 ml 2% HCl + 5 g KBr	11·15	1·129
6	10·0	10·0	50 ml 2% HCl + 7·5 g KBr	11·65	1·583
7	10·0	10·0	50 ml 20% HCl + 2·5 g KBr	10·62	0·363
8	10·0	10·0	50 ml 20% HCl + 5 g KBr	10·42	0·569
9	10·0	10·0	50 ml 20% HCl + 7·5 g KBr	10·69	0·791
10	10·0	10·0	50 ml 20% HCl + 5 g KBr (double precipitation)	10·02	0·007
11	10·0	10·0	(double precipitation)	10·03	0·007
12	10·0	10·0	(double precipitation)	10·08	0·005

TABLE V.—PRECIPITATION OF IRIDIUM USING A SLURRY OF CALOMEL IN THE PRESENCE OF IODIDE

Test	Iridium taken, *mg*	Conditions of precipitation using mercury[I] chloride slurry	Iridium found radiometrically in the precipitate, *mg*
1	10·0	100 ml 10% HCl + 5 g KBr + 5 g KI	9·53
2	10·0	200 ml 10% HCl + 5 g KBr + 5 g KI	9·00
3	10·0	300 ml 10% HCl + 5 g KBr + 5 g KI	5·37
4	10·0	200 ml 10% HCl + 5 g KI	9·72
5	10·0	200 ml 10% HCl + 5 g KI	9·71
6	10·0	200 ml 10% HCl + 10 g KI	5·92
7	10·0	200 ml 10% HCl + 15 g KI	4·23
8	10·0	200 ml 10% HCl + 20 g KI	2·82
9	10·0	200 ml 5% HCl + 10 g KBr + 10 g KI	6·57
10	10·0	200 ml 10% HCl + 10 g KBr + 10 g KI	5·52
11	10·0	200 ml 20% HCl + 10 g KBr + 10 g KI	5·68
12	10·0	200 ml 10% HCl + 10 g KBr + 1 g KI	5·27
13	10·0	200 ml 10% HCl + 10 g KBr + 3 g KI	10·11
14	10·0	200 ml 10% HCl + 10 g KBr + 5 g KI	10·17
15	10·0	200 ml 10% HCl + 10 g KBr + 5 g KI	10·09
16	10·0	200 ml 10% HCl + 5 g KBr + 5 g KI	10·07
17	10·0	200 ml 10% HCl + 5 g NaBr + 5 g KI	9·98
18	10·0	200 ml 10% HCl + 10 g NaBr + 5 g KI	10·04

recovered as the volume of the solution and the acid concentration were increased. Five g of potassium iodide appeared to be sufficient for the reaction, but the presence of bromide was found to assist in the recovery of the iridium (Table V). It was observed that in order to obtain complete recovery, it was necessary to boil the solutions until the colour changed from brown to black.

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Iridium was not precipitated from solutions containing iodide by the addition of mercury^{II} chloride and hypophosphorous acid.

ANALYTICAL PROCEDURE FOR THE SEPARATION AND DETERMINATION OF MILLIGRAM QUANTITIES OF RHODIUM AND IRIDIUM

Relatively few convenient and satisfactory methods for the separation and subsequent determination of rhodium and iridium have been reported.[6,8–12] The following new procedure is proposed on the basis of the present study.

A sample solution should not contain more than 0·1 g of rhodium and iridium as chloride complexes, and oxidising acids must be absent.

TABLE VI.—SEPARATION AND GRAVIMETRIC DETERMINATION OF RHODIUM AND IRIDIUM

Test	Rhodium taken, *mg*	Iridium taken, *mg*	Conditions of separation using mercury^{I} chloride slurry	Iridium found gravimetrically *mg*	Rhodium found gravimetrically *mg*	Iridium in recovered rhodium, *mg*
1	10·0	10·0	50 ml 20% HCl + 5 g KBr, + 5 g KI (for Ir)	10·05	10·06	0·005
2	10·0	10·0	50 ml 20% HCl + 5 g KBr, + 5 g KI (for Ir)	10·02	10·19	0·005
3	30·0	30·0	100 ml 20% HCl + 10 g KBr, + 5 g KI (for Ir)	30·56	29·79	0·008
4	30·0	30·0	100 ml 20% HCl + 10 g KBr, + 5 g KI (for Ir)	30·55	29·83	0·006

Procedure

Dilute the solution in a 400-ml beaker to 100 ml with 20% (v/v) hydrochloric acid and add 10 g of potassium bromide. Boil gently, and add a slurry of mercury^{I} chloride until all of the rhodium has been precipitated (indicated by the presence of an excess of white calomel). Continue boiling, with stirring, until the rhodium coagulates and settles rapidly. Filter through a 9-cm Whatman No. 44 filter and wash the precipitate well with 2% hydrochloric acid. Retain the filtrate for the determination of iridium.

Dissolve the precipitate of rhodium on the paper with hot brominated hydrochloric acid and wash it into the original beaker. Evaporate the resulting solution to *ca.* 2 ml and dilute to 100 ml with 20% (v/v) hydrochloric acid. Add 10 g of sodium bromide and precipitate rhodium with mercury^{I} chloride slurry as before. Filter and wash the precipitate with hot 2% hydrochloric acid. Retain the filtrate for the determination of iridium.

Heat the precipitate of rhodium gently in a porcelain crucible in an efficient fume-cupboard to burn off the filter paper and volatilise mercury. Then heat for 30 min at 1000° in an electric muffle-furnace. Reduce the residue of rhodium in hydrogen, cool and weigh.

Combine the filtrates containing the iridium and evaporate to 200 ml. Add 5 g of potassium iodide, boil gently, and add an excess of mercury^{I} chloride slurry. Boil until the colour changes from brown to black. Allow the precipitate to settle. Filter, wash, ignite at 900°, reduce in hydrogen and weigh the resultant iridium as for the rhodium.

Results of tests of the procedure show that the separation and recovery of the metals is satisfactory, and that very little iridium is detectable in the recovered rhodium (Table VI).

Zusammenfassung—Iridium-192 wurde als Tracer verwendet um die Trennung von Platin und Rhodium von Iridium mittels Mercurochlorid oder Mercurichlorid und hypophosphoriger Säure als selective Fällungsmittel zu studieren. Es wurde gefunden, dass beide Reagenzien eine befriedigende Trennung von Platin und Iridium gestatten. In Gegenwart von Bromid kann Rhodium von Iridium getrennt werden durch Fällung mittels einer Aufschlämmung von Mercurochlorid. Iridium wird durch diese Aufschlämmung quantitative gefällt, wenn Iodid anwesend ist. Eine neue Schnellmethode zur Trennung von Rhodium und Iridium und anschliessenden Bestimmung der beiden Metalle wird vorgeschlagen.

Résumé—L'iridium 192 a été utilisé comme traceur dans une étude de séparation du platine et du rhodium d'une part et de l'iridium d'autre part, le chlorure mercureux ou le chlorure mercurique et l'acide hypophosphoreux étant utilisés comme précipitant sélectif. Les auteurs ont trouvé que le platine peut être séparé de l'iridium de façon satisfaisante par l'utilisation de l'un ou l'autre de ces composés. En présence de bromure, le rhodium peut être séparé convenablement de l'iridium par une précipitation utilisant une pâte de chlorure mercureux. L'iridium peut être précipité quantitativement par cette pâte si de l'iodure est présent. Une nouvelle méthode rapide de séparation du rhodium et de l'iridium et le dosage subséquent de ces deux métaux sont proposés.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—II

THE CHLORAMINE-T–ARSENIC^{III} REACTION A POTENTIOMETRIC STUDY

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Summary—A potentiometric study has been made of the titration of arsenic^{III} with chloramine-T under a very wide range of conditions in order to establish the limits within which the reaction is quantitative and analytically acceptable, and also to gain an insight into the mechanism of the reaction. It has been established that, in the absence of added halide, chloramine-T oxidises arsenic^{III} either extremely slowly in strong acid solution or not at all at lower hydrogen ion concentrations. In the presence of chloride, the reaction is satisfactory with a chloride concentration greater than 0·5*M* and in hydrogen ion concentrations over the range 0·5 to 5·0*M*. In the presence of bromide at a final concentration of 0·1*M*, the reaction is quantitative over a hydrogen ion concentration range of $10^{-5}M$ to 5·0*M*; and in the presence of iodide to a final amount of 0·005*M* the results are excellent in the pH range of 4 to 9. In the presence of bromide or iodide the range can be extended to slightly higher pH limits by increasing the halide concentration. The actual oxidising species is hydrogen ion-independent, but subject to katagenic action by halide ion, and is probably free halogen. The use of diluted titrant solutions for determining small quantities of arsenic^{III} (about 0·1 mmole) at high dilution does not afford any marked improvement in accuracy.

THE chloramine-T–arsenic^{III} reaction is of fundamental importance in two ways. First, arsenious oxide is a primary, if not an ultimate, standard, and may be used for standardisation of chloramine-T solutions.[1] Upon the accuracy of this reaction, therefore, rests the accuracy of all other titrimetric determinations with chloramine-T. Second, many substances are not amenable to direct or reverse titration with chloramine-T, either because the reaction is incomplete or too slow, or because suitable indication of the end-point is lacking. In such cases it is often possible to make the reaction rapid and quantitative by using an excess of chloramine-T, followed by destruction of that excess by the addition of arsenic^{III} solution, the excess of which is finally determined by continuation of the titration with the original chloramine-T solution. This technique[2] is termed "double-excess back-titration".

Consequently, this reaction has been subjected to the closest scrutiny, and the conditions of reaction varied over a very wide range in order to define their limits, without neglecting detailed examination of conditions intermediate between the limits so that any anomalies, such as arise in the bromate–antimony^{III} reaction, may not escape detection. Since this is the most widely applicable reaction, it has been used for the development and assessment of new indicators, and of new techniques such as differential electrolytic potentiometry.[3]

Previous accounts of the reaction tend to be vague and inadequate, giving rise to ambiguity and uncertainty. Thus, arsenic^{III} has been

(a) titrated in bicarbonate solution[4] containing some potassium iodide and using

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starch as indicator. The amount of iodide has not been examined, nor has the possibility of using other buffers in place of sodium bicarbonate.

(b) titrated in "neutral" solution (*i.e.* without the addition of buffers, acids or alkalis) at an elevated, but unspecified temperature either potentiometrically[5] or using starch-iodide paper[6] as external indicator.

(c) titrated potentiometrically in hydrochloric acid.[7,8] The most suitable acid concentration is uncertain.

(d) titrated in hydrochloric acid using the visual indicators methyl red,[8] brilliant carmoisine[9] and *p*-ethoxychrysoïdine.[9] Titrations with methyl red were carried out at an elevated, but unspecified temperature in 1·0*M* acid. Titrations using brilliant carmoisine and *p*-ethoxychrysoïdine were carried out in 5% concentrated hydrochloric acid at room temperature.

Only in the case of methyl red[8] has the end-point been checked by the recognised criterion of potentiometric titration. Since most indicators incur an appreciable titration error, this is an important omission. The data presented here will be used for this purpose in a subsequent paper[13] describing work with visual indicators. In the present paper, the detailed potentiometric study of the oxidation of arsenic^{III} is described and the results are briefly discussed only as far as they affect the present determination.

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EXPERIMENTAL

Apparatus and reagents

The apparatus and most of the reagents have been previously described.[1] Additional reagents are specified below. Checks on the theoretical titre were made by 50-ml titrations using the methods previously outlined[1] and confirmed by potentiometric titration under the optimum conditions.[1]

0·05*M* *arsenic^{III} solution, free from chloride:* prepared, for the titrations in sulphuric acid media, as previously described, except that sulphuric instead of hydrochloric acid was used to acidify the alkaline arsenite solution, the final acid concentration being about 0·05*M*.

Potassium bromide: AnalaR reagent, free from bromate, other oxidising agents and iodide, but containing approximately 0·15% of chloride, was used to prepare a stock 1·0*M* solution.

Stock buffer solutions: AnalaR compounds were used to prepare the stock solutions. The volume of solution or weight of solid added to the titration solution, and the pH measured with a glass electrode at the end of the titration in a volume of 200 ml are given in parentheses.

Bicarbonate—One mole of sodium bicarbonate dissolved, by prolonged stirring, in 900 ml of cold water, then diluted to 1 litre. (80 ml, pH 8·0).

Borax—Solid borax decahydrate was used. (3·8 g ≡ final concentration of 0·05*M*, pH 8·9).

Sodium carbonate—Solid anhydrous sodium carbonate was used. (2·1 g ≡ final concentration of 0·1*M*, pH 10·4).

Acetate—A solution 0·6*M* in sodium acetate and 1·4*M* in acetic acid. (50 ml, pH 4·2).

Phosphate—A solution 0·233*M* in disodium hydrogen phosphate and 0·1*M* in potassium dihydrogen phosphate. (40 ml, pH 6·2).

Phthalate—0·2*M* potassium hydrogen phthalate. (50 ml plus 15 ml of 0·5*M* hydrochloric acid, pH 2·3; 50 ml plus 10 ml of 0·5*M* hydrochloric acid, pH 2·5).

Procedure

The volume of titration solution was fixed to be 200 ml at the equivalence point, and quantities of acid, potassium halide, etc., sufficient to give the quoted concentrations at the equivalence point were initially added. In diluting the solution with halide-free distilled water to begin the titration, due allowance was made for the amount of wash water used during titration. The latter quantity was determined by averaging the amount used over a number of trial runs, and led to a final deviation in equivalence point volume of about ±2%. In passing through the end-point, increments of titrant were added split-dropwise, by allowing a drop partially to form, removing this from the burette tip with a clean, but moist glass rod, then washing into the titration beaker. Potentials were taken to be

in equilibrium when the rate of drift fell below 1 mV per min. Generally, potentials reached equilibrium through the end-point in less than 5 min, and after the end-point in less than 3 min. When equilibration was slower than this, it was usually very much slower, and in such circumstances readings were taken at 15-min intervals, except in the cases noted where the potential was rising slowly at the equivalence point, when a period up to several hr if necessary was allowed. When the potentials were "hunting", that is drifting slowly about in an aimless fashion, as happens before the equivalence point with an irreversible reductant, readings were taken at 5-min intervals. Normally

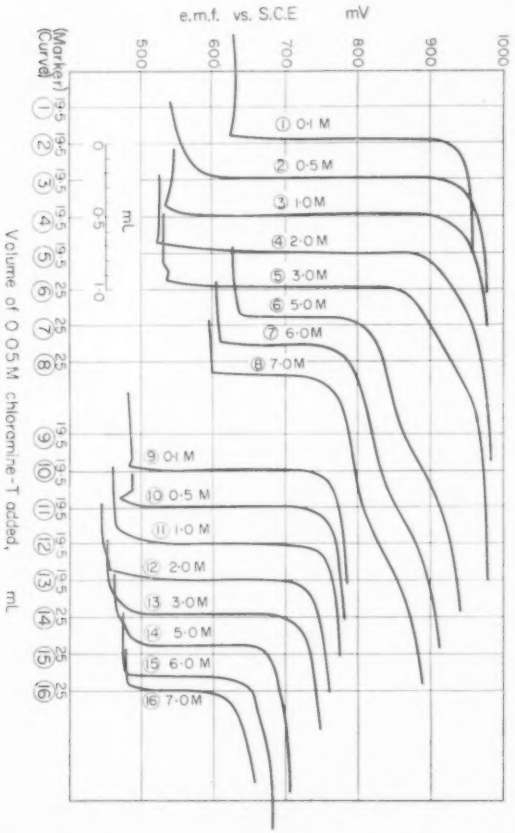

FIG. 1. Titrations in hydrochloric acid media.
Curves 1–8, HCl alone
Curves 9–16, in 0·1*M* bromide.

the portion of the curve within ±1 ml (±4%) of the end-point was carefully studied, but where exploratory titrations indicated further features of interest, e.g. a second inflection, the range was appropriately extended. Although only one curve is illustrated under each set of conditions and the figures in the tables refer to the single result from each curve, curves and end-points were checked by replication, usually in triplicate, and all showed excellent reproducibility of potentials (within 2–5 mV) and of end-points (within a titrimetric error of ±0·016 ml or ±0·06%).

RESULTS AND DISCUSSION

Reaction in hydrochloric acid media

(a) *Alone.* Curves are shown in Fig. 1 for titrations over the range 0·1 to 7·0*M* hydrochloric acid. All gave satisfactory end-points, but in the titration at 0·1*M* hydrochloric acid, the equilibration of potential was so slow as to render the titration impracticable. At higher acid concentrations equilibration was reasonably rapid, though the potentials were unsteady before the end-point in acid concentrations below

3·0*M*, as is to be expected with an irreversible reductant. Above 3·0*M* hydrochloric acid, the pre-end-point potentials became quite steady.

The results in Table I indicate that the end- and equivalence points are in satisfactory agreement over the range of 0·5 to 5·0*M* hydrochloric acid. Below 0·5*M* acid, the end-point is premature and the reaction is incomplete and extremely slow. Above 5·0*M* acid, the end-points become progressively earlier due to a shift in the redox equilibrium at high hydrogen ion concentrations.

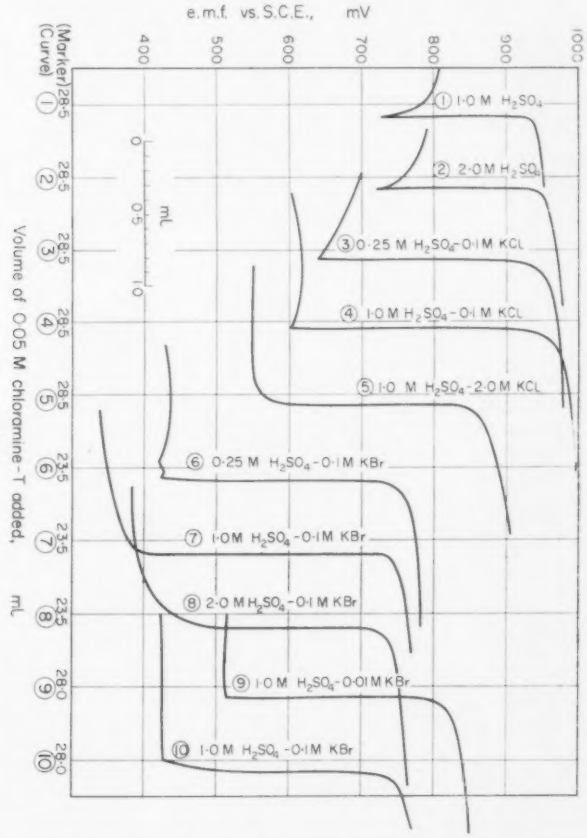

FIG. 2. Titrations in sulphuric acid media.
Curves 1–2, H_2SO_4 alone
Curves 3–5, in presence of chloride
Curves 6–10, in presence of bromide.

(b) *In the presence of* 0·1*M bromide.* With a bromide concentration of 0·1*M* at the equivalence point, excellent end-points were obtained over a range of hydrochloric acid concentrations from 0·1*M* to 7·0*M* as the curves 9 to 16 in Fig. 1 show. Equilibration of potential was rapid in all cases, and the pre-end-point potentials were steadier than in the absence of bromide, though the improvement with increasing acid concentration was not so marked. The accuracy is good from 0·1 to 5·0*M* hydrochloric acid, but at higher acid concentrations oxidation of bromide by arsenic^{V} gives rise to negative errors.

Reactions in sulphuric acid media

(a) *Alone.* Curves 1 and 2 in Fig. 2 and the results in Table 1 appear to be quite satisfactory but, in fact, the reaction was extremely slow; the points for the curves

were recorded at 15-min intervals and there was no real end-point—merely a slow increase in potential on long standing at the noted end-points. In 0·25*M* sulphuric acid the reaction, if any, was so slow that no curve could be derived. In the presence of excess chloramine-T, however, the potentials came to equilibrium quite quickly, presumably due to the formation of chloride of concentration $2 \times 10^{-3}M$ by decomposition of the chloramine-T.

(b) *In the presence of added chloride.* With a chloride concentration of 0·1*M* at the equivalence point it was possible to obtain a curve in 0·25*M* sulphuric acid, although the rate of potential rise at the end-point was still very slow. Increasing the sulphuric acid concentration to 1·0*M* gave a much more rapid, but slightly premature, rise at the end-point. By increasing the chloride concentration to 2·0*M* with the same sulphuric acid concentration satisfactory curves, equilibration speeds and end-points were produced, and the solution became green due to the liberation of chlorine after the end-point.

The presence of both hydrogen and halide ion is therefore necessary before the reaction becomes analytically useful.

(c) *In the presence of added bromide.* With a bromide concentration of 0·1*M* at the equivalence point, titration in the range of sulphuric acid concentration from 0·25*M* to 2·0*M* gave excellent end-points in close agreement with theory, and bromine was liberated immediately after the end-point. With a bromide concentration of 0·01*M* equally good results were achieved at higher potentials. Although the potentials were again unsteady on the reduced side, the equilibration rate was rapid at and beyond the end-point.

Reaction in buffer media

(a) *Alone, and in the presence of added chloride.* In 0·025*M* chloride the reaction was extremely and impracticably slow at pH 2·5, and the reaction ceased entirely at higher pH values and in the absence of added halide.

(b) *In the presence of added bromide.* With an equivalence point concentration of 0·1*M* bromide, satisfactory curves (1 and 2, Fig. 3) and results (Table I) were achieved at pH 2·5 and pH 4·2; the end-point was late at pH 6·2 and the reaction had ceased entirely at pH 8. On the grounds that the late end-point at the upper pH limit of the reaction is due to hydrolysis of the free halogen which is the active oxidant,[1] an increase in the halide concentration should afford an improvement. An increase in bromide concentration to 1·0*M* at the equivalence point does, in fact, give considerable improvement at pH 6·1 (curve 4, Fig. 3, and Table I), but at higher pH values the reaction becomes too slow to be practicable. It is also notable that the appearance of the colour of free bromine after the end-point is delayed at higher pH values, being 0·5 ml after the end-point at pH 4·2 in 0·1*M* bromide and at pH 6·1 in 1·0*M* bromide: at pH 6·2 in 0·1*M* bromide a 100% excess of oxidant was required before the colour appeared. Potential equilibration at the end-point became very slow in 0·1*M* bromide at pH 6·2, but rapid equilibration was restored on increasing the bromide concentration to 1·0*M*.

(c) *In the presence of added iodide.* Curves 5 to 10 of Fig. 3 illustrate the effects of variation of pH over the range 2·3 to 10·6 in the presence of iodide at concentrations of 0·05 to 0·0005*M* at the equivalence point. Titrations were satisfactory from pH 4 to

pH 8·9 in 0·005*M* iodide and the results (Table I) were accurate. Although the end-point appears to be satisfactory at pH 2·5, the reaction is too slow to be analytically useful, and a decrease in iodide concentration to 0·0005*M* in order to increase the redox potential did not significantly increase the rate of oxidation of the arsenic. The accuracy of the results is probably misleading, since negative errors may be expected to arise at such pH values due to the beginning of the shift in equilibrium in

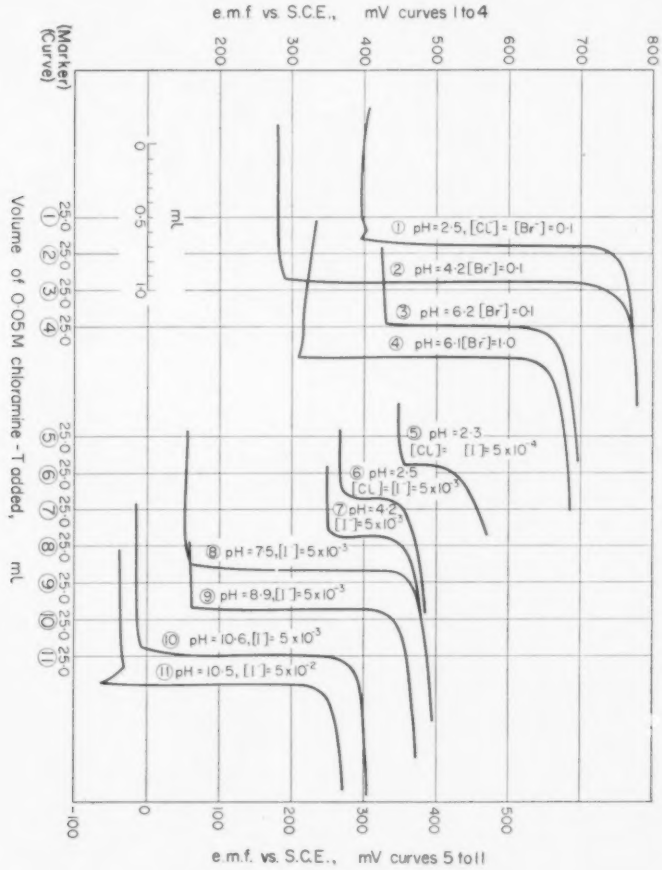

FIG. 3. Titrations in buffer media.

the iodine–arsenic^{III} reaction towards incomplete oxidation of the arsenic^{III}, but the slowness of the reaction tends to conceal this. A marked lateness in end-point appears at pH 10·6 due to hydrolysis of the iodine,[1] and the accuracy may once again be improved by increasing the iodide concentration to suppress hydrolysis. An increase of iodide concentration to 0·05*M* reduces, but does not entirely eliminate, the error. At and above pH 4, equilibration of the potentials was rapid at and beyond the end-point, but as usual the potentials were unsteady on the reduced side. At very high pH values, the reaction again ceases entirely.

It is therefore evident that the oxidising action of chloramine-T is rather specific, and is confined to restricted ranges of hydrogen ion concentration. In the absence of

TABLE I.—POTENTIOMETRIC TITRATION OF APPROXIMATELY 0·005*M* As^{III} WITH 0·05*M* CHLORAMINE-T UNDER VARIOUS CONDITIONS

Conditions								Titre		Error	
Concentrations at the equivalence point, *M*											
Fig.	Curve	HCl	H_2SO_4	Buffer pH	KCl	KBr	KI	Theory	Found	*ml*	%
1	1	0·1	—	—	—	—	—	19·75	19·72	−0·03	−0·17
	2	0·5	—	—	—	—	—	19·75	19·74	−0·01	−0·05
	3	1·0	—	—	—	—	—	19·75	19·73	−0·02	−0·10
	4	2·0	—	—	—	—	—	19·75	19·75	0	0
	5	3·0	—	—	—	—	—	19·75	19·725	−0·025	−0·13
	6	5·0	—	—	—	—	—	25·18	25·185	+0·005	+0·02
	7	6·0	—	—	—	—	—	25·18	25·125	−0·055	−0·22
	8	7·0	—	—	—	—	—	25·18	25·09	−0·09	−0·36
	9	0·1	—	—	—	0·1	—	19·75	19·74	−0·01	−0·05
	10	0·5	—	—	—	0·1	—	19·75	19·74	−0·01	−0·05
	11	1·0	—	—	—	0·1	—	19·75	19·75	0	0
	12	2·0	—	—	—	0·1	—	19·75	19·75	0	0
	13	3·0	—	—	—	0·1	—	19·75	19·725	−0·025	−0·13
	14	5·0	—	—	—	0·1	—	25·18	25·18	0	0
	15	6·0	—	—	—	0·1	—	25·18	25·15	−0·03	−0·12
	16	7·0	—	—	—	0·1	—	25·18	25·00	−0·18	−0·72
2	1	—	1·0	—	—	—	—	28·58	28·58	0	0
	2	—	2·0	—	—	—	—	28·58	28·575	−0·005	−0·02
	3	—	0·25	—	0·1	—	—	28·58	28·565	−0·015	−0·05
	4	—	1·0	—	0·1	—	—	28·58	28·55	−0·03	−0·10
	5	—	1·0	—	2·0	—	—	28·58	28·57	−0·01	−0·04
	6	—	0·25	—	—	0·1	—	23·59	23·595	+0·005	+0·02
	7	—	1·0	—	—	0·1	—	23·59	23·60	+0·01	+0·04
	10	—	1·0	—	—	0·1	—	28·08	28·085	+0·005	+0·02
	8	—	2·0	—	—	0·1	—	23·59	23·595	+0·005	+0·02
	9	—	1·0	—	—	0·01	—	28·08	28·07	−0·01	−0·04
3	1	—	—	2·5	—	0·1	—	25·18	25·19	+0·01	+0·04
	2	—	—	4·2	—	0·1	—	25·18	25·20	+0·02	+0·08
	3	—	—	6·2	—	0·1	—	25·18	25·25	+0·07	+0·28
	4	—	—	6·1	—	1·0	—	25·18	25·21	+0·03	+0·12
	5	—	—	2·3	—	—	0·0005	25·18	25·20	+0·02	+0·08
	6	—	—	2·5	—	—	0·005	25·18	25·17	−0·01	−0·04
	7	—	—	4·2	—	—	0·005	25·18	25·18	0	0
	8	—	—	7·7	—	—	0·005	25·18	25·17	−0·01	−0·04
	9	—	—	8·9	—	—	0·005	25·18	25·18	0	0
	10	—	—	10·6	—	—	0·005	25·18	25·24	+0·06	+0·24
	11	—	—	10·5	—	—	0·05	25·18	25·20	+0·02	+0·08

added halide, no reaction at all occurs at low acidities, while at high acidities the reaction is extremely slow, different in character from the normal reaction, and probably dependent on small amounts of chloride either initially present as impurity in the reagent or formed by its decomposition. In the presence of chloride ion, the reaction becomes impracticably slow and the end-point premature when the chloride ion concentration falls to 0·1*M* in strong acid solution. In the presence of hydrochloric acid the minimum practicable concentration is 0·5*M*, while the maximum concentration is 5·0*M*. In more concentrated solutions the end-points become premature due to the influence of hydrogen ion on the As^{III}/As^{V} potential. In the presence of bromide, chloramine-T is a satisfactory oxidant over the range of hydrogen ion concentration 5·0 to $10^{-5}M$ at a bromide concentration of 0·1*M*. At higher hydrogen ion concentrations the arsenic potential rises sufficiently to prevent complete reaction, and at lower concentrations the reaction becomes slow or ceases altogether. At the same time hydrolysis of bromine occurs, leading to late end-points, though this effect can be diminished by increasing the bromide concentration to 1·0*M* at a hydrogen ion concentration of $10^{-6}M$. In the presence of iodide, an upper limit is set to the permissible hydrogen ion concentration for the oxidation of arsenic^{III} by the oxidation of iodide by arsenic^{V}, which is first evidenced by a rapid decline in the speed of reaction. A lower limit is set by hydrolysis of the iodine produced as an intermediate. The practicable range is from pH 4 to pH 9 at an iodide concentration of 0·005*M*. An increase in the iodide concentration to 0·05*M* permits extension of the lower limit to pH 10.

Chloramine-T, therefore, although it has a high apparent redox potential, is incapable of effective reaction in the absence of added halide. In the presence of chloride it will react at a hydrogen ion concentration above 0·5*M*; in the presence of bromide this limit is extended to $10^{-5}M$, the upper limit of 5·0*M* being set in the titration of arsenic^{III} by partial reversal of the reaction between free halogen and arsenic^{III} at high hydrogen ion concentrations. In the presence of iodide, chloramine-T will react down to pH 9 or even pH 10, an upper limit in the case of oxidation of arsenic^{III} being set at about pH 4. It is also notable that the minimal requirement in respect to the concentration of added halide decreases with decreasing redox potential of the halide, being about 0·5*M* for chloride, 0·01*M* for bromide and 0·005*M* for iodide. Catalysts such as osmic acid, vanadates, molybdates or tungstates are without influence.

Titration at low reagent concentration

Titrations under most of the conditions described above were also made with ten-fold diluted reagents (0·0005*M* arsenic^{III} and 0·005*M* chloramine-T); the curves are shown in Fig. 4 and the results in Table II. In all cases the end-point was late, generally to the extent of about 0·4%, but at a bromide concentration of 0·1*M* the error increased to about 1·5%.

In hydrochloric acid alone, the rise in potential through the end-point at 0·5*M* was very slow, but improved at higher concentrations. The same was true in lesser degree in the presence of 0·01*M* bromide. An increase of bromide concentration to 0·1*M* gave rise to peculiar curves. At all acid concentrations the potential started to climb slowly after the equivalence point, but there was no sharp rise until the recorded end-point, some 0·4 ml after the equivalence point. At this stage the potentials

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reached equilibrium quickly and the colour of free bromine became apparent. The double inflections which may be sensed in all the curves become apparent in the presence of 0·01*M* bromide, though no additional error is introduced if the first rising inflection is taken as the end-point. The most satisfactory titration is considered to be that in bicarbonate buffer with an iodide concentration of 0·005*M*. Although the end-point is still more than 0·3% late, the potentials were steady and reached

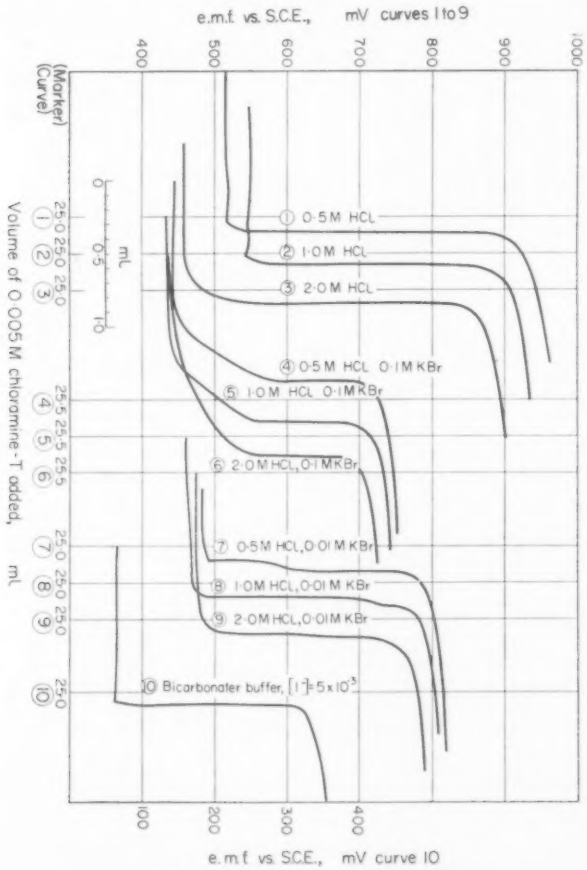

FIG. 4.—Titrations at ten-fold dilution.

equilibrium quickly. Titrations with visual indicators gave similar results, as will be shown in a subsequent paper,[13] confirming that, although there is a slight improvement in precision (replicability), there is no improvement in accuracy when using diluted titrant. The same accuracy of 0·4% is achieved in a titration requiring either 25 ml of 0·005*M* titrant or 2·5 ml of 0·05*M* titrant. Chloramine-T shares this phenomenon with many other titrimetric reagents.

Interpretation of curves

Full discussion of curve forms and potentials will be deferred until all of the data for the various reactions have been presented, but certain salient features of the curves for the arsenic^{III} reaction may be underlined at this time.

(*a*) In all cases the form of the curve and the behaviour of the potentials before the end-point is typical of an irreversible redox system. This is fully confirmed by the differential electrolytic potentiometric curves.[3]

(*b*) The form of the curves through and after the end-point indicates a high degree of reversibility in the oxidant system. Many curves (*e.g.* curves 3, 4, 5, Fig. 1) illustrate how the oxidant system picks up control of the potential just before the end-point.[11]

(*c*) The curvature on the oxidant side of the end-point under analytically useful

TABLE II.—POTENTIOMETRIC TITRATION OF APPROXIMATELY 0·0005*M* As^{III} WITH 0·005*M* CHLORAMINE-T UNDER VARIOUS CONDITIONS

Conditions	Titre,* *ml*	Error	
		ml	%
0·5*M* HCl	25·10	+0·10	+0·40
1·0*M* HCl	25·075	+0·075	+0·30
2·0*M* HCl	25·09	+0·09	+0·36
0·5*M* HCl + 0·1*M* KBr	25·38	+0·38	+1·52
1·0*M* HCl + 0·1*M* KBr	25·405	+0·40	+1·60
2·0*M* HCl + 0·1*M* KBr	25·37	+0·37	+1·48
0·5*M* HCl + 0·01*M* KBr	25·10	+0·10	+0·40
1·0*M* HCl + 0·01*M* KBr	25·10	+0·10	+0·40
2·0*M* HCl + 0·01*M* KBr	25·09	+0·09	+0·36
Bicarbonate buffer + 0·005*M* KI	25·08	+0·08	+0·32

* Theoretical titre, 25·00 ml.

conditions fits extremely well with the value $n = 2$ for the number of electrons transferred in the reaction

$$ox + n\varepsilon = red.$$

(*d*) The value of the potentials on the oxidant side does not rise with increasing hydrogen ion concentration. In view of the reversibility of the oxidant reaction, the potential-determining redox species cannot, therefore, involve hydrogen ion in its reaction. Chloramine-T, dichloramine-T, the free acid RNHCl, hypochlorous acid or hypochlorite ion are not, therefore, the actual reacting species.

(*e*) The potentials after the end-point fall with increasing halide concentration. A net katagenic ion is, therefore, involved in the redox reaction, and this ion must be a halide ion.

(*f*) Confirmation of the contention that hydrolysis of the free halogen supervenes at the lower useful limit of hydrogen ion concentration for each halide is given by the drop in potential which occurs in each case as well as by the slowness in equilibration of the potentials.

(*g*) In the absence of added halide (Fig. 2, curves 1 and 2), the curvature corresponds to a value of $n = 4$ for the number of electrons transferred, and such other deviations from $n = 2$ as do occur are to be found in chloride media.

(*h*) The development of a second inflection in high hydrochloric acid concentrations

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is well illustrated in curves 4 to 8 in Fig. 1. These do not affect the first inflection or the analytical results, and will be shown to be due to traces of a titratable substance in the hydrochloric acid.

CONCLUSIONS

Chloramine-T, as a titrimetric reagent, reacts through reaction-intermediates which are probably free halogens, and fails to react under circumstances which preclude the generation of such intermediates, as in the absence of added halide, or when the concentration of such halide is so low that the primary redox potential of chloramine-T is not high enough to generate sufficient free halogen to afford a satisfactory reaction. It has been shown elsewhere[12] that free halogen produced slowly or in minute quantity fails as an oxidant due to hydrolysis, even in acid media. Consequently, minimal requirements in halide ion concentration have to be met. Under the appropriate conditions of hydrogen and halide ion concentrations, the oxidation of arsenic^{III} by chloramine-T is quantitative.

Zusammenfassung—Eine potentiometrische Studie wurde unternommen, um den Verlauf der Reaktion zwischen Arsen(III) und Chloramin T zu Klären und in weitem Bereich die Grenzen für die Anwendbarkeit dieser Reaktion zur Bestimmung von Arsen aufzufinden. Es wurde gefunden, dass in Abwesenheit von Halogensalzen das Arsen in stark saurer Lösung nur äusserst langsam oxydiert wird und in schwach saurer Lösung überhaupt nicht. In Gegenwart von Chloride (höher als 0·5 m) und einer H-Ionenkonzentration von 0·5–5·0 m verläuft die Reaktion zufriedenstellend. In Gegenwart von Bromid (Endkonzentration 0·1 m) ist die Reaktion quantitativ bei einer H-Ionenkonzentration 10^{-5}–5·0 m. In Anwesenheit von Jodid (Endkonzentration 0·005 m) werden ausgezeichnete Resultate erhalten im pH Bereich 4–9. Im Falle von Bromid und Jodid kann die pH-Grenze etwas nach der alkalischen Seite verschoben werden, wenn höhere Halogenkonzentration eingestellt werden. Die tatsächlich oxydierende Komponente ist ph-unabhängig, unterliegt aber katagenen Einflüssen durch die Halogenionen, und ist vermutlich freies Halogen. Die Verwendung stark verdünnter Masslösungen zur Bestimmung kleiner Arsenmengen (ca 0·1 Millimol) in hochverdünnten Lösungen ergibt keinen nennenswerten Anstieg der Genauigkeit.

Résumé—Les auteurs ont fait une étude potentiométrique du titrage de l'arsenic(III) par la chloramine T dans un très large domaine de conditions afin d'établir les limites dans lesquelles la réaction est quantitative et acceptable au point de vue analytique, et d'obtenir une connaissance du mécanisme de la réaction. Il a été établi que, en l'absence d'halogenures ajoutés, la chloramine T oxyde l'arsenic (III) soit extremement lentement en milieu acide fort, soit pas du tout pour les concentrations en ions hydrogène plus faibles. En présence de chlorure, la réaction est satisfaisante avec une concentration de chlorure supérieure à 0,5*M* et des concentrations en ion hydrogène comprises dans le domaine 0,5*M* à 5*M*. En présence de bromure, à une concentration finale 0,1*M*, la réaction est quantitative dans un domaine de concentration d'ion hydrogène de $10^{-5}M$ à 5*M*, et en présence d'iodure en concentration finale 0,005*M*, les résultats sont excellents dans le domaine de pH 4–9. En présence de bromure ou d'iodure le domaine peut être étendu à limites de pH légèrement plus élevées en augmentant la concentration d'halogénure. L'espèce oxydante réelle est indépendante de l'ion hydrogène, mais est sujette à l'action catagénique de l'ion halogénure et est probablement de l'halogène libre. L'utilisation de solutions diluées titrantes pour doser de faibles quantités d'arsenic (III) (environ 0,1 mole) à grande dilution n'apporte pas d'amélioration marquée de la précision.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—III

THE CHLORAMINE-T–ARSENIC^{III} REACTION A STUDY OF VISUAL INDICATORS

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Summary—A search has been made for visual indicators suitable for application in chloramine-T titrimetry, and ten compounds, five reversible and five irreversible, have been rigorously examined in the titration of arsenic^{III} under conditions for which the titrimetric reaction has been shown to be quantitative. Indicator errors have been checked by direct comparison with potentiometric titrations under similar conditions. Recommendations have been made as to the best media, and indicators have been arranged in order of preference under various conditions. Titrations at a ten-fold dilution of the customary concentration have been investigated and found to offer no advantage.

THE fundamental importance of the chloramine-T–arsenic^{III} reaction in respect to the standardisation[1] and analytical application[2] of chloramine-T has already been emphasised. The reaction has been subjected to a comprehensive potentiometric investigation[2] and the quantitative limits under various conditions have been defined. From the summary already made[2] of the conditions under which arsenic^{III} has previously been titrated with chloramine-T, it is evident that few good visual indicators are available for this titration. Apart from starch which, as it requires the presence of iodide, may not always be used, only methyl red,[3] methyl orange,[4] brilliant carmoisine[5] and *p*-ethoxychrysoïdine[5] have previously been recommended. Of these, only starch and *p*-ethoxychrysoïdine show reversibility, though the reversibility of the latter, which has been recognised in arsenic^{III}–bromate titrations, has not thus far been examined in the case of chloramine-T.

Of those indicators which have been used in chloramine-T titrimetry, methyl red alone[3] has been subjected to checking by the recognised criterion of potentiometric titration. This is an important omission, because visual indicators often incur an appreciable titration error. Poethke and Wolf[5] have attempted to assess the indicator errors for brilliant carmoisine and *p*-ethoxychrysoïdine, by conducting a blank titration on the pure indicator solution. Although this method has also been included in the present work, it is open to suspicion as it may not take into account such factors as the character and speed of the main and indicator reactions, induced and side reactions and concentration effects. Consequently the preferred method, used here, is direct comparison with potentiometric titrations[2] under the same conditions.

Since the chloramine-T–arsenic^{III} reaction has been so thoroughly investigated[1,2] it has been used as the test reaction for the development and examination of new indicators as well as for the critical re-assessment of those previously recommended. Substances for test as possible indicators were selected on the following grounds:

(*a*) Known reactivity to free halogen. Substances already in use as indicators in

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bromate, iodate and hypochlorite titrimetry were an obvious first choice. Other substances reported to have a poor fastness to chlorine[6] were also tried, but most proved to be unsatisfactory, either because of a poor or indistinct colour change or because they were so poorly resistant that they were prematurely destroyed.

(*b*) Known redox indicator properties. Of other known redox indicators, *o*-dianisidine[7] alone proved to have suitable characteristics.

(*c*) From a survey of several thousand dyestuffs and related materials for indicator properties,[8] those which showed the best reactivity to bromate were examined. Of these, which are mainly substitution products of pararosaniline, the best was rosaniline.

(*d*) Specific reagents for free halogen. These include rosaniline and α-naphthoflavone for bromine and starch and its derivatives for iodine.

Of the indicators finally selected for exhaustive testing, methyl orange, methyl red and *p*-ethoxychrysoïdine have previously received some attention, but the remainder, rosaniline,[1] bordeaux,[9] amaranth,[10] quinoline yellow,[11] *o*-dianisidine,[7] tartrazine,[12] and α-naphthoflavone[13] have not been applied to chloramine-T titrimetry. Of these, *p*-ethoxychrysoïdine, quinoline yellow, *o*-dianisidine, tartrazine and α-naphthoflavone show reversibility under certain conditions.

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Rosaniline has already been carefully examined[1] and found to yield accurate results with a negligible ($< 0{\cdot}01$ ml) correction in media 0·5 to 2·5*M* in hydrochloric acid and 0·01 to 0·1*M* in potassium bromide. The chloramine-T–arsenic^{III} reaction has also been shown[2] to be quantitative (*a*) in the presence of a minimum chloride concentration of 0·5*M* over the range of hydrogen ion concentration of 0·5 to 5·0*M*, (*b*) in the presence of 0·01 to 0·1*M* bromide at hydrogen ion concentrations between 10^{-5} and 5·0*M*, and (*c*) in the presence of 0·005*M* iodide within the pH range 4 to 9. Errors arising in visual indicator titrations under these conditions may therefore be ascribed to the indicator.

EXPERIMENTAL

Apparatus and reagents

These have already been described.[1,2] Arsenic^{III} solutions for use in sulphuric acid media were prepared by the alternative method.[2] The source of material, strength and method of preparation of indicator solutions are shown in Table I. Normally 2 drops of the indicator solution per 100 ml of titration solution were used, except in the cases of starch and α-naphthoflavone where 1 ml was added.

Procedures

A detailed account has been given.[16] Volumetric glassware was used in the manner already described,[17] titrations were completed split-dropwise,[1,2] allowing 15–30 sec between the addition of each increment. All titrations were conducted at room temperature and the results corrected to 20°. The method given for rosaniline[1] was employed with the other irreversible indicators. Reversibility, where appropriate, was checked by adding a known amount, 5 or 10 ml, of arsenic^{III} solution, warming or allowing the mixture to stand until the original colour was fully restored, and titrating to a second end-point. The concentrations of reagents recorded refer to the equivalence point volume of the titration solution, and in diluting the mixture before starting the titration, due allowance was made for the amount of wash water used. Except for the second end-points with reversible indicators, the equivalence point volume was normally 100 ml ± 5%.

RESULTS

Indicator blanks

Table II shows the results of titrations of 1 ml of the indicator solution in various media at a dilution of 100 ml with 0·005*M* chloramine-T. These figures must be

TABLE I.—INDICATORS

Compound	Source and grade	British Colour Index number	Strength of solution	Method of preparing solution
Starch	AnalaR	—	1% aqueous solution	1 g solid to 100 ml boiling water. Solution boiled for 2 min and cooled before use. Solution prepared daily.
Rosaniline hydrochloride	Hopkin & Williams Ltd.	677	0·1% in 0·02*M* hydrochloric acid	0·1 g dissolved in 100 ml warm 0·02*M* hydrochloric acid solution, cooled and decanted.
Methyl orange	AnalaR	142	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
Methyl red (sodium salt)	Hopkin & Williams Ltd. pH indicator	211	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
Bordeaux	Hopkin & Williams Ltd. Revector dye	88	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
Amaranth	British Drug Houses Ltd. Technical Dye	184	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
p-Ethoxychrysoïdine	Hopkin & Williams Ltd. Redox Indicator	—	0·1% aqueous solution	0·1 g added to 100 ml boiling water, cooled and decanted.
Quinoline yellow	I.C.I. Ltd. Dyestuff	801	0·5% aqueous solution	0·5 g dissolved in 100 ml water.
o-Dianisidine	Hopkin & Williams Ltd.	—	0·2% in 2*M* acetic acid	0·2 g dissolved in 12 ml glacial acetic acid and diluted to 100 ml with water.
Tartrazine	Hopkin & Williams Ltd. Adsorption Indicator	640	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
α-Naphthoflavone	Hopkin & Williams Ltd.	—	0·1% ethyl alcohol solution	0·1 g dissolved in 100 ml absolute ethyl alcohol.

accepted with considerable reservations as noted above, but they may serve roughly to indicate the relative blanks. Apart from α-naphthoflavone, where 1 ml is required, the amount of indicator used in normal titrations is less than 0·2 ml, so that the indicator error should be one fiftieth of the blank shown in the table. Most of the indicators should have a measurable error which is smallest in hydrochloric acid free from other halides. Induction, however, tends to reduce this error in practice, and under conditions for which the main reaction is slow, appreciable fading of the indicator colour occurs before the end-point, or else the more easily destroyed indicators yield premature end-points.

TABLE II.—TITRATION OF 1·0 ML OF INDICATOR SOLUTIONS IN 100 ML OF VARIOUS MEDIA WITH 0·005*M* CHLORAMINE-T

Indicator	Colour change	Vol. of 0·005*M* chloramine-T required to produce colour change, *ml*		
		1·0*M* HCl	1·0*M* HCl + 0·1*M* KBr	1·0*M* H_2SO_4 + 0·1*M* KBr
Rosaniline	yellow–purple	—	0·3	0·3
Methyl orange	red–pale yellow	1·0	2·0	1·5
Methyl red	crimson–pale yellow	1·0	2·7	1·8
Bordeaux	crimson–pale yellow	0·8	0·8	0·8
Amaranth	crimson–pale yellow	0·7	0·8	0·8
p-Ethoxychrysoïdine	orange–yellow	1·3	1·2	1·2
Quinoline yellow	yellow–colourless	1·2	2·0	2·0
o-Dianisidine	colourless–orange red	0·2	0·3	0·3
Tartrazine	yellow–colourless	1·3	—	—
α-Naphthoflavone	(colloidal) white–yellow	—	0·1	0·1

Indicator errors and suitability in various media

Results of titrations in equivalence point volumes of 100 ml of the various media in which the reaction is known to be quantitative[2] are shown in Table III. The indicator errors shown are the differences between replicate visual titrations and titrations conducted potentiometrically under similar conditions.[2] As previously observed,[2] 0·5*M* hydrochloric acid in the absence of bromide is a minimal condition under which the reaction between chloramine-T and arsenic^{III} is slowing down, and it is therefore not surprising that all of the indicators give positive errors of considerable magnitude.

Specific reagents for free bromine are not, of course, applicable in the absence of bromide, and quinoline yellow was prematurely decolorised under the same conditions. Tartrazine failed to show any reversibility to a further addition of 5 ml of arsenic solution after the first colour change, and *p*-ethoxychrysoïdine did not give a pleasing second end-point. *o*-Dianisidine reversed satisfactorily and gave excellent second end-points in 1·0 and 2·0*M* hydrochloric acid, and so it is recommended for use in these media. The other indicators are subject to irreversible colour changes. Methyl orange, methyl red and tartrazine show appreciable titration errors at all

hydrochloric acid concentrations, but in 1·0 and 2·0*M* hydrochloric acid the errors were negligible with bordeaux, amaranth, *p*-ethoxychrysoïdine and *o*-dianisidine, so that these indicators are recommended for this titration.

In hydrochloric acid media in the presence of bromide in a concentration of 0·1*M*, tartrazine was not oxidised by the bromine formed at the end-point. The specific reagents for free bromine gave excellent results, and α-naphthoflavone is furthermore reversible. The other indicators generally show a greater positive error in the presence of bromide and, except for *p*-ethoxychrysoïdine, the error increases with an increasing hydrochloric acid concentration. In addition to rosaniline, bordeaux, amaranth and

TABLE III.—INDICATOR ERRORS INCURRED IN THE TITRATION OF 20 OR 25 ML OF 0·05*M* ARSENIC^{III} IN VARIOUS MEDIA WITH 0·05*M* CHLORAMINE-T

Indicator	Error, *ml*, in titration in							
	0·5*M* HCl	1·0*M* HCl	2·0*M* HCl	0·5*M* HCl + 0·1*M* KBr	1·0*M* HCl + 0·1*M* KBr	2·0*M* HCl + 0·1*M* KBr	1·0*M* H_2SO_4 + 0·1*M* KBr	Acetate buffer pH = 4·1 + 0·1*M* KBr
Rosaniline	—	—	—	0·00	0·00	0·00	0·00	—
Methyl orange	+0·06	+0·02	+0·02	+0·02	+0·04	+0·06	+0·04	+0·06
Methyl red	+0·05	+0·02	+0·02	+0·02	+0·04	+0·06	+0·05	+0·04
Bordeaux	+0·03	0·00	0·00	+0·02	+0·02	+0·04	0·00	+0·06
Amaranth	+0·03	0·00	0·00	0·00	+0·00	+0·02	0·00	+0·04
p-Ethoxy-chrysoïdine	+0·05	0·00	0·00	+0·05	+0·03	+0·02	+0·01	—
(2nd end-point)	—	0·00	0·00	+0·02	+0·01	0·00	+0·02	—
Quinoline yellow	—	—	—	+0·06	+0·04	+0·06	+0·03	+0·06
(2nd end-point)	—	—	—	+0·02	+0·01	—	+0·06	+0·05
o-Dianisidine	+0·04	0·00	0·00	+0·02	+0·03	+0·03	0·00	—
(2nd end-point)	—	0·00	0·00	0·00	+0·03	+0·02	—	—
Tartrazine	+0·06	+0·02	+0·02	—	—	—	—	+0·06
(2nd end-point)	—	—	—	—	—	—	—	+0·05
α-Naphtho-flavone	—	—	—	0·00	0·00	+0·01	0·00	—
(2nd end-point)	—	—	—	−0·01	−0·01	−0·01	+0·03	—

Volume of solution at the equivalence point, 100 ml. Two drops of indicator solution per 100 ml added, except for α-naphthoflavone, when 1·0 ml of indicator solution per 100 ml added. Where a second end-point is recorded, this was taken after a further addition of 5 or 10 ml of 0·05*M* arsenic^{III} solution.

α-naphthoflavone are recommended for use in these media since they give the most accurate and pleasing end-points. Although the error is rather large, and the second colour change rather poor, *p*-ethoxychrysoïdine, quinoline yellow (in 1·0*M* hydrochloric acid) and *o*-dianisidine have the advantage of being reversible.

In chloride-free sulphuric acid solution of concentrations 0·25, 0·5, 1·0, 1·5 and 2·0*M*, rosaniline in the presence of 0·1*M* bromide gave excellent end-points with no detectable indicator error. The sharpest and most pleasing colour changes occurred in 1·0 and 1·5*M* sulphuric acid; in 0·25 and 0·5*M* acid, the purple colour developed rather slowly at the end-point and in 2·0*M* acid the colour was a little pale. Decreasing the bromide concentration to 0·01*M* did not affect the quality or accuracy of the end-point. Other indicators were examined at the optimum sulphuric acid concentration and in 0·1*M* bromide. The reaction in the absence of added bromide was too slow to permit the use of visual indicators. In general, the indicator errors are smaller in sulphuric than in hydrochloric acid media. Bordeaux and amaranth gave

both accurate and pleasing results and are particularly recommended. Methyl orange and methyl red gave sharp and pleasing, though late end-points. *p*-Ethoxychrysoïdine and quinoline yellow both showed reversibility to further additions of arsenic^{III} solution, quinoline yellow being more satisfactory, but *o*-dianisidine and α-naphthoflavone, although giving very satisfactory first end-points, did not reverse well.

At a pH of 4, only in the presence of bromide is the titration analytically useful,[2] so that the indicator titrations were conducted in acetate buffer with a bromide concentration of 0·1*M*. Rosaniline, *p*-ethoxychrysoïdine, *o*-dianisidine and α-naphthoflavone changed long before the equivalence point and are therefore unsuitable.

TABLE IV.—INDICATOR ERRORS INCURRED IN THE TITRATION OF 25 ML OF 0·0005*M* ARSENIC^{III} IN VARIOUS MEDIA WITH 0·005*M* CHLORAMINE-T

Indicator	Conditions	Total error, *ml*	Error due to indicator, *ml*
Amaranth	0·5*M* HCl	+0·19	+0·09
	1·0*M* HCl	+0·11	+0·06
	2·0*M* HCl	+0·12	+0·04
Rosaniline	0·5*M* HCl + 0·1*M* KBr	—	
	1·0*M* HCl + 0·1*M* KBr	—	
	2·0*M* HCl + 0·1*M* KBr	—	
	0·5*M* HCl + 0·01*M* KBr	+0·14	−0·01
	1·0*M* HCl + 0·01*M* KBr	+0·12	+0·01
	2·0*M* HCl + 0·01*M* KBr	+0·12	+0·01
Starch	0·4*M* $NaHCO_3$ + 0·005*M* KI	+0·11	+0·03
	0·4*M* $NaHCO_3$ + 0·025*M* KI	+0·10	+0·02

Volume of solution at the equivalence point, 100 ml. 1·0 ml starch or 2 drops of amaranth or rosaniline indicator solution per 100 ml added. Results in column 4 are corrected for the inherent error in the determination.[2]

Methyl orange, methyl red, bordeaux and amaranth were subject to fading before the end-point and so gave poor—and late—colour changes. Quinoline yellow and, surprisingly, tartrazine gave sharp, though considerably late, end-points, and both showed excellent reversibility and are therefore recommended.

Titrations at low reagent concentration

Titrations at a ten-fold overall dilution are subject to a net positive error[2] of about 0·4%. With visual indicators this error is increased, and the total error is shown in Table IV. By subtracting the known titration error,[2] the net contribution of the indicator to the total error is obtained. This is greatest in 0·5*M* hydrochloric acid and decreases with rising acid concentration. The net error is least with rosaniline in the presence of 0·01*M* bromide and greatest with amaranth in hydrochloric acid alone. In hydrochloric acid, the amaranth colour change was fairly sharp in 1·0 and 2·0*M* acid, but rather slow in 0·5*M* acid. In the presence of 0·1*M* bromide, the rosaniline colour developed very slowly (compare the lower part of the potentiometric curves under these conditions[2]) and no satisfactory end-point could be discerned. A reduction of the bromide concentration to 0·01*M* effected a very considerable improvement,

but the end-points were still not quite so sharp as with amaranth in the absence of bromide. The net error with starch in bicarbonate buffer in the presence of iodide is intermediate between those of amaranth and rosaniline, and the end-points were marked by the sharp appearance of a very pale blue colour. These titrations confirm the findings by potentiometric titration[2] that no advantage pertains to the use of a diluted reagent in titrating small quantities of arsenic^{III}, since the error, of about 0·4%, is similar to the precision attained in a titration of 2·5 ml with a reagent of ordinary strength. With the aid of a microburette and potentiometric location of the end-point, indeed, the stronger reagent is the more advantageous. Where titrations with 0·005*M* chloramine-T are conducted, however, it is considered that all three indicators are suitable in their respective media, starch being the best.

Conclusions and discussion

In judging the performance of a particular indicator, three factors are relevant: (*a*) the indicator error,[14] shown in the tables, (*b*) the sharpness of the colour change, and (*c*) the quality (brightness, intensity, contrast) of the colour change. Although factor (*a*) is of prime importance, an indicator with a very sharp, highly contrasting colour change may be acceptable even if it shows a high error, provided the latter is perfectly reproducible.

Among the indicators which have proved suitable for chloramine-T titrimetry are examples of several types[15] of redox indicator:—

Reversible redox indicators: *o*-dianisidine, whose oxidation mechanism has been fully elucidated;[7,10] *p*-ethoxychrysoïdine and quinoline yellow which operate through a conjugation mechanism: the redox mechanism of tartrazine is uncertain.

Irreversible dyestuffs: methyl red, methyl orange, bordeaux and amaranth, which are irreversibly oxidised or destroyed with the formation of very weakly coloured products.

Specific sensitive reagents: starch for iodine and α-naphthoflavone for bromine, which react reversibly forming coloured addition products with free halogen in the presence of halide ion. Both are colloidal in nature, the yellow bromine addition product with α-naphthoflavone often flocculating on formation. Rosaniline reacts with free bromine[8] with the formation of deep purple polybromo compounds, the bromine atoms, in average number 4, entering the positions ortho to the nitrogen atoms. The compound is also colloidal and very sparingly soluble.

The irreversible indicators, to be satisfactory, must react more slowly than the reductant so that a local excess of titrant does not give premature end-points. For the same reason, the addition of the indicator should be delayed to as near the end-point as possible. The indicators examined, particularly amaranth and bordeaux, were reasonably satisfactory in this respect. The brilliant colour change and negligible indicator error of rosaniline make it a particularly valuable indicator despite the inconvenience of its irreversibility, and the difficulty experienced the first time the indicator is used.

The quality of the colour change is outstandingly good for rosaniline, good for amaranth and bordeaux and, where there is no fading, for methyl red and methyl orange. *o*-Dianisidine gives a good colour change and is the best of the reversible indicators, *p*-ethoxychrysoïdine, tartrazine and quinoline yellow have poor colour changes, and quinoline yellow is subject to a sudden fading of the yellow colour just

before the end-point. The colour change of α-naphthoflavone is fair in colourless solutions, but sometimes difficult to discern otherwise.

In general, only amaranth and the specific reagents for bromine stand up to the presence of bromide, the other indicators being better in hydrochloric acid alone. The substitution of sulphuric for hydrochloric acid in the presence of bromide yields a general improvement in quality and accuracy, the best end-points of all, on all counts, being with rosaniline in 1·0 to 1·5*M* sulphuric acid and 0·01 to 0·1*M* bromide.

Balancing all three factors and taking reversibility into account, the following recommendations are made:

(*a*) In hydrochloric acid at 1·0 to 2·0*M* concentration, amaranth, bordeaux and *o*-dianisidine are the best; *p*-ethoxychrysoïdine is also suitable as are methyl red and methyl orange subject to a correction of −0·02 ml.

(*b*) In hydrochloric acid at 1·0 to 2·0*M* concentration in the presence of 0·1*M* bromide, rosaniline is outstandingly good. Amaranth is also recommended, and α-naphthoflavone, though the colour change is not brilliant, is accurate and reversible. Other indicators are useful though the error is rather high.

(*c*) In 1·0*M* sulphuric acid in the presence of 0·01 to 0·1*M* bromide, rosaniline is pre-eminent, amaranth and bordeaux are excellent, and the quality of the end-point is good with both methyl red and methyl orange although the error is very high. Of the reversible indicators quinoline yellow is the most satisfactory, followed by *p*-ethoxychrysoïdine.

(*d*) In acetate buffer in the presence of 0·1*M* bromide, few indicators give satisfactory results, the best, despite high errors, being quinoline yellow and tartrazine, which have the advantage of reversibility.

(*e*) Sulphuric acid in the presence of bromide is the medium which offers the most pleasing end-points, 1·0 to 2·0*M* hydrochloric acid yields the smallest errors, and acetate buffer media are not recommended.

(*f*) A titration with 0·005*M* chloramine-T offers no advantage. At this dilution, starch in the presence of iodide in bicarbonate buffer gives the best end-points, but both amaranth in hydrochloric acid and rosaniline in hydrochloric acid media containing bromide at a concentration of 0·01*M* are acceptable.

Zusammenfassung—Es wurde nach visuellen Indicatoren für die Chloramin-T-Titration gesucht. Zehn Verbindungen, fünf reversibel und fünf irreversibel reagierend, wurden einer genauen Untersuchung unterzogen, und zwar unter Bedingungen, unter denen die Reaktion zwischen Chloaramin-T und Arsen(III) quantitativ verläuft. Indicatorfehler wurden studiert durch direkten Vergleich mit potentiometrischen Titrationen unter gleichen Bedingungen. Die bestgeeigneten Bedingungen werden beschrieben und die Indicatoren in der Reihenfolge bester Eignung aufgezählt. Titrationen mit Lösungen in zehnfacher Verdünnung der üblichen Titrationslösungen wurden durchgeführt, doch ergab sich keinerlei Vorteil.

Résumé—Les auteurs ont fait une recherche d'indicateurs visuels convenables pour l'application á la titrimétrie de la chloramine T; dix composés, cinq réversibles et cinq irréversibles, ont été examinés de manière rigoureuse dans le titrage de l'arsenic(III) dans les conditions pour lesquelles on a montré que la réaction de titrage était quantitative.

Les erreurs dues à l'indicateur ont été vérifiées par comparaison directe avec des titrages potentiométriques dans des conditions semblables. Des recommandations ont été données sur les meilleurs milieux, et les indicateurs ont été rangés par ordre de préférence dans diverses conditions. Des titrages ont été étudiés pour une dilution égale au dixième de la concentration usuelle, mais ils n'offrent aucun avantage.

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DETERMINATION OF TUNGSTEN IN ASSOCIATION WITH IRON AND SOME OTHER ELEMENTS AS TRIS(TRI-n-BUTYLAMMONIUM)12-TUNGSTOPHOSPHATE

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Summary—Conversion of tungsten into 12-tungstophosphoric acid for determination with tri-n-butylamine requires acidification of an alkaline solution containing tungstate and phosphate. Complications associated with the presence of large amounts of iron have been resolved by adsorbing tungstophosphoric acid from 6*N* hydrochloric acid on a column of cellulose, which does not adsorb iron^{III} chloride. The conditions of formation of the heteropolyacid that lead to its quantitative retention are critical and a little iron seems to be bound with the tungsten. After the adsorbate has been removed from the column, its minor iron content can be rendered innocuous by reduction before precipitation of tris(tri-n-butylammonium)12-tungstophosphate. The effect of several other elements has been briefly studied.

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TUNGSTEN in the form of 12-tungstophosphoric acid can be determined as tris(tri-n-butylammonium)12-tungstophosphate in the presence of considerable amounts of calcium, cobalt^{II}, copper, lead, manganese^{II} and nickel,[1] but iron[2] and some other elements may exert a pronounced adverse effect. The primary object of this investigation was to find a means of determining tungsten in materials containing iron and a limited number of other elements, the production of 12-tungstophosphoric acid being required in their presence.

Apparently the only satisfactory method of forming tungstophosphoric acid is to acidify alkaline solutions containing tungstate and phosphate. Moderate amounts of the specified elements, except iron, and a *small* amount of iron^{II} can then be tolerated. Ascorbic acid is a suitable reductant for iron^{III} and for subsidiary amounts of cobalt^{III} and manganese^{III} formed in alkaline solutions.

We have found that authentic 12-tungstophosphoric acid is strongly adsorbed by cellulose from 6*N* hydrochloric acid solutions and separable from iron^{III} by a column procedure. However, the heteropolyacid obtained from tungstate in the presence of phosphate and iron behaves differently and, under conditions in which the tungsten is quantitatively retained by a column of cellulose, a little iron is also held. When tungsten has been eluted from the column and tungstophosphoric acid reformed, the accompanying iron can be reduced with ascorbic acid before tributylamine is added.

Methods have been developed for determination of tungsten in a few selected materials.

EXPERIMENTAL

Reagents

Johnson, Matthey's tungsten metal powder (>99·9%), spectrographically standardised tungsten^{VI} oxide (99·99%) and iron sponge, AnalaR sodium tungstate and 12-tungstophosphoric acid, and Hilger's "specpure" solutions of tantalum and niobium fluorides were used. As far as possible other reagents were analytical-reagent grade. The tungsten content of anhydrous sodium tungstate was

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checked with reference to the tungsten^{VI} oxide. Tri-n-butylamine was purified as before.[1] Sodium hydroxide solutions were stored in polythene bottles. The concentrated hydrochloric acid was 12*N*.

Apparatus

6-, 10- and 25-Ml platinum crucibles with lids were used for various operations. Polytetrafluoroethylene beakers, covers and stirring rods permitted the use of hydrofluoric acid with *aqua regia*.

Notes on methods

Unless otherwise stated, all determinations of tungsten as tris(tri-n-butylammonium)12-tungstophosphate relate to precipitates formed in 1*N* hydrochloric acid solutions and left overnight before filtration.[1]

Small amounts of tungsten in effluents and filtrates were detected and estimated semi-quantitatively, essentially as described by Miller,[3] except that the zinc complex of toluene-3:4-dithiol[4] ("dithiol") was used. Portions of solutions containing tributylammonium salts were evaporated to dryness, with the aid of an air current, in a boiling water-bath, *not* on a hot-plate. Ascorbic acid did not upset the reaction.

DETERMINATION OF TUNGSTOPHORIC ACID DERIVED FROM TUNGSTEN

In the presence of just sufficient (0·6 ml) orthophosphoric acid (sp. gr. 1·75) to prevent the separation of tungstic acid at a later stage, 200-mg amounts of tungsten powder were oxidised with nitric acid along with either hydrochloric or hydrofluoric acid. The quantities of hydrochloric and nitric acids were so chosen that, after the reaction had ceased, the addition of 90 ml of water gave an approximately 1*N* hydrochloric acid solution. Hydrofluoric acid was expelled by heating the platinum crucible containing the reactants within a metal block which was heated finally at 180°. Water was used to transfer the syrupy residue to a beaker and hydrochloric acid added. Precipitation and separation of the tributylamine complex were then effected.

By the *aqua regia* method, apparent recoveries of tungsten were 99·9 and 100·1% with, however, 0·4% in the filtrates, whereas by the hydrofluoric acid method, 99·0, 99·3 and 100·4% were obtained, with 0·5, 0·8 and 0·1% in the respective filtrates. Residual fluoride was probably not responsible for the low recovery of tungsten in two precipitates since, when 160 mg of sodium fluoride were added to a solution of 12-tungstophosphoric acid, the determination of tungsten was little affected, no doubt because the glassware reacted with the fluoride. When a polythene beaker was used there was, however, a marked negative error.

In three further experiments involving the use of hydrofluoric and nitric acids, increasing amounts of sodium hydroxide solution were added to the aqueous extracts of the phosphoric acid residues in order to raise the pH to 9·6, 10 and >10. The solutions were acidified with 6*N* hydrochloric acid before the addition of the amine. The tungsten in the precipitates correspondingly increased from 99·3 to 100·0% of that originally taken and that in the filtrates decreased from 0·4 to 0·2%.

It was concluded that, for the satisfactory formation of 12-tungstophosphoric acid from materials disintegrated with acids, it would be necessary, in order to break down all tungsten complexes, to make the solutions strongly alkaline, then re-acidify them. Since precipitated tungstic acid dissolves readily in sodium hydroxide solution, it would be superfluous to add phosphoric acid initially. Instead, sulphuric acid could be used and less phosphate, if desired, added afterwards to the alkaline solution. The

influence of elements that had previously been found not to upset the determination of 12-tungstophosphoric acid, when they were added to acidified solutions, had now to be found when the solutions containing them were made alkaline, then re-acidified. A few additional elements were included in the tests.

Effect of other elements

Solutions of chlorides (nitrate for lead) of various elements were added to solutions containing 200 mg of tungsten^{VI}, which were then made strongly alkaline

TABLE I—EFFECT OF VARIOUS ELEMENTS ON THE DETERMINATION OF TUNGSTEN

Element	Amount added, *mg*	Tungsten calculated, %	Tungsten in filtrate, %
Calcium	200	99·9	0·7
	200*	100·5	<0·1
	50*	99·9	<0·4
Cobalt^{II}	200†	100·4	0
Copper^{II}	200	100·6	0
Lead	200	100·2	n.d.
Manganese^{II}	200	102·3	0·2
	200†	100·1	<0·1
Nickel	200	100·2	<0·1
Aluminium	100	98·5	1·2
Tin^{IV}	25	100·6	0·3
Titanium^{IV}	10	105·8	1·5
Tantalum^{V} + niobium^{V}	5 + 5	104·8	0·4

* Sulphate present
† Ascorbic acid added

with sodium hydroxide solution. 43 Mg of phosphate (PO_4) were added, the heated stirred solutions were gradually acidified with concentrated hydrochloric acid (nitric acid for lead) and tungsten was determined. Tantalum and niobium fluorides were added to a solution prepared by dissolving 200 mg of tungsten in hydrofluoric, nitric and sulphuric acids. The first two acids were expelled and the residue was made alkaline, *etc.* as above. A precipitate, presumably of tantalic and niobic acids, was collected in a sintered-glass filter crucible when the volume of the solution was 40 ml and the acid concentration 1*N*.

The results given in Table I show that titanium, tantalum and niobium interfere seriously. Chromium^{III}, molybdenum^{VI} and vanadium^{V} were also known to interfere.[1] Interference caused at first by manganese resulted from its oxidation in alkaline solution, but 100 mg of ascorbic acid added to the re-acidified solution eliminated the error. Such reduction was also useful for some cobalt^{III}.

Influence of iron

For the determination of 200 mg of tungsten^{VI} as above in the presence of 100 mg of iron^{III}, the re-acidified solution was reduced in a silver reductor and precipitation with tributylamine effected in 2*N* hydrochloric acid.[2] Although the apparent recovery of tungsten in the precipitate was 99·5%, 1% was found in the filtrate. Ascorbic acid,

if used in a large excess, was a suitable reductant for *small* amounts of iron^{III}. 100 Mg added to re-acidified solutions containing tungstate and iron^{III} counteracted the interference of up to 2 mg of the latter in the subsequent determination of tungsten with tributylamine in 1*N* hydrochloric acid solution. When 5-25 mg of iron were present, iron-contaminated precipitates of tributylammonium tungstophosphate were obtained.

ELIMINATION OF INTERFERENCE OF LARGER AMOUNTS OF IRON

12-Tungstophosphoric acid was found to be strongly adsorbed by filter paper from moderately concentrated hydrochloric, nitric and sulphuric acid solutions. When a

Table II—Adsorption behaviour of authentic 12-tungstophosphoric acid
(200 mg of tungsten)

Hydrochloric acid present in applied solution and eluent, *N*	Other components of the applied solution, *mg*	Tungsten found in successive 50-ml portions of effluent, *mg*	
		Original solution unheated	Original solution boiled for 20 min and cooled before use
6	—	0·1, 0, 0, 0	1·1, 0·3 (25 ml tested)
6	850, PO_4 (as H_3PO_4)	0·15, 0	3·5, 0
6	200, iron	0·3, 0, 0	—
6	200, iron; 850, PO_4	0·3, 0	—
2	—	0·15, 0·1	<0·2, 0, 0·15
2	200, iron	8, 0·3, 0	—

spot of a hydrochloric acid solution, containing 25 μg of tungsten as the heteropoly-acid and 25 μg of iron^{III}, was applied near the top of a paper strip and a chromatogram developed with 6*N* hydrochloric acid as the mobile phase, iron travelled just behind the solvent front and tungsten was detected[5] at the starting position. In 3*N* acid, tungsten gave two bands, with R_F values 0 and 0·06, and iron behaved as before. These results suggested a possible means of separating tungstate from iron.

Adsorption of 12*-tungstophosphoric acid by cellulose*

Glass columns (15-mm internal diameter) containing cellulose, derived from a suspension of Whatman ashless, standard-grade cellulose powder (6 g) in water, were made up and the behaviour thereon of 30 ml of solutions of varied composition, prepared from solid 12-tungstophosphoric acid, was studied. Solutions were added to columns pre-treated with acid of the same strength as that of the sample and a flow-rate of 3-5 ml per min was used, suction or light pressure being applied when necessary. 17–20 Ml of liquid (the retention volume of the column) were rejected, then liquid was continuously collected as the solution passed into the cellulose and the column was washed with acid of the requisite strength. Successive portions of effluent were tested qualitatively for tungsten, with the results shown in Table II. After use, the columns were freed from tungstate by washing them with water, 0·2*N* sodium hydroxide solution and again with water.

12-Tungstophosphoric acid is obviously strongly held by cellulose. In unheated 6*N* hydrochloric acid an excess of phosphate did not influence the behaviour and the

effect of iron was slight, but in boiled solutions the initial expulsion of a significant amount of tungsten occurred. Only in acid of the higher concentration was tungsten adequately withheld in the presence of iron^{III} which was not retained by the cellulose. Chromium^{III} behaved like iron^{III}. The presence of hydrofluoric acid hindered the adsorption of tungsten. 12-Tungstosilicic, 12-tungstoboric, 18-tungsto-2-phosphoric and 12-molybdophosphoric acids were also adsorbed by cellulose from 6*N* hydrochloric acid.

Tentative experiments on the adsorption of tungstophosphoric acid prepared from tungsten

50–80-Mg amounts of tungsten, alone or in presence of 12 mg of iron, were dissolved and oxidised in the three ways outlined on p. 44, except that 0·3 ml of orthophosphoric acid was used and volumes were kept down so as to give 6–15 ml of 6*N* hydrochloric acid solutions for application to columns of cellulose. The column procedure was the same as before, 6*N* hydrochloric acid being used for elution and portions of effluent being tested for tungsten.

Generally, a sharp initial expulsion of a few mg of tungsten occurred. Thereafter, a slight continuous loss of tungsten was noted, the loss being least where *aqua regia* had been used to dissolve tungsten. When iron was present, the bulk was soon eluted but a little "tailed" on the column and could not be expelled with an amount of hydrochloric acid that did not also cause more significant loss of tungsten.

More promising results with respect to retention of tungsten were obtained when hydrofluoric and nitric acids were used and phosphoric acid was replaced by sulphuric acid, which permitted more certain removal of hydrofluoric acid and avoided possible complications arising from the formation of polyphosphoric acids. Thereafter the suspension of tungstic acid was made alkaline, then phosphate and acid were added. Further experiments with 200 mg of tungsten plus 50–200 mg of iron indicated that the quantity of sulphuric acid was not critical, but that the amount of phosphate had to be small and the rate of acidification rapid. Quantitative separation of iron from tungsten seemed to be impossible, but the small amount left with tungsten was amenable to treatment with ascorbic acid (p. 45) before determination of the tungsten.

Critical investigation of the formation and adsorption behaviour of tungstophosphoric acid

In a series of experiments, 20–25 ml of solutions, containing sodium tungstate, disodium hydrogen phosphate and sufficient sodium hydroxide to give a blue colour with thymol blue indicator, were swirled or magnetically stirred while hydrochloric acid was added fairly quickly dropwise from a burette until the indicator was red. The volumes of the cold solutions were then doubled by the rapid dropwise addition of 12*N* hydrochloric acid. The solutions were applied as before to columns containing 6 g of cellulose, equilibrated with 6*N* hydrochloric acid, and elution was effected with that acid. The results given in Table III show that the neutralisation of hot solutions with 12*N* acid almost prevented any loss of tungsten in the first fraction of effluent. The tungsten contents of subsequent fractions showed that a high concentration of phosphate and, to a much smaller extent, a high concentration of neutralising acid accelerated the travel of tungsten on the column. The use of more cellulose might have improved matters.

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In further experiments, 0·3 ml of concentrated sulphuric acid, 4 ml of 12*N* sodium hydroxide solution and 43 mg of phosphate (PO_4) were added in succession to tungstate solutions, which were then heated to 80°. Thereupon 12*N* hydrochloric acid was added from a burette at a much faster rate than before to rapidly stirred solutions until the pH was 4, 2 or 1. Solutions were maintained hot for 5 min, cooled, treated with the same volume of 12*N* acid, re-cooled and transferred to columns, *etc.* 100 Ml of column effluent yielded 0·1 mg of tungsten for the first two experiments and

TABLE III—LOSS OF TUNGSTEN FROM COLUMNS TO WHICH TUNGSTOPHOSPHORIC ACID PREPARED FROM 200 mg OF TUNGSTEN^{VI} AND PHOSPHATE HAD BEEN APPLIED

(200 mg of W ≡ 8·5 mg of PO_4)

Phosphate (PO_4), *mg*	17	17	17	17	17	43	85	850	850	850
HCl for neutralisation, *N*	2	2	6	6	12	6	6	2	2	12
Approx. temp. when neutralised, °*C*	18	100	100	100	100	100	100	18	100	100
Volume applied to column, *ml*	50	50	50	30	50	50	50	60	60	60
Tungsten in successive 50-ml portions of effluent, *mg*	2 0·4 0·2	0·5 <0·1 0·2	0·2 <0·1 0·3	0·2 <0·1 0·5	0 0·7 1·5	0·8 0·4 1·5	0·4 2 6	4 20 16	1 15 11	0·3 40 20

0·3 mg for the last. The difference was insignificant and it was concluded that even the very rapid addition of acid was permissible up to and beyond the point at which the formation of 12-tungstophosphoric acid might be considered complete.[6] Overnight delay before or after increasing the acidity to 6*N* did not influence the column behaviour of tungsten.

Effect of iron

The above experiments were repeated, but with iron^{III} sulphate (100 mg of iron) in sulphuric acid solution added to the tungstate just before the sodium hydroxide. The mixture was heated to 80°, then phosphate and acid were added. It was difficult to stop at exactly pH 4 or 2 and simplest to stop the addition of acid when hydrated iron^{III} oxide was significantly dissolving (pH < 1). Continued heating at this stage assisted solution. In several experiments about 0·2 mg of tungsten was collected in the first 50 ml of column effluent, but 2–6 mg in the next. The travel of tungstophosphoric acid had been accelerated in the presence of iron. A column containing 10 g of cellulose reduced the loss of tungsten in 100 ml of effluent to 0·2 mg. This loss was unchanged when 200 mg of iron^{III} and 17–43 mg of phosphate (PO_4) were used but rose to 1·2 mg with 430 mg of phosphate, thus confirming the harmful influence of a large quantity. In all experiments a minor amount of iron remained with the tungsten.

DETERMINATION OF TUNGSTEN IN ASSOCIATION WITH IRON

Preparation of columns and conditions of use

A 24-cm length of Pyrex glass tubing (about 20-mm internal diameter) was sealed close to the barrel of a capillary stopcock of which the full length of capillary below the tap was retained. The

base of the column was so constructed that a perforated disc of nearly the same diameter as the column could be readily seated, leaving minimum free space below it. On the disc a circle of Whatman No. 41 filter paper was placed. More uniform packing of the column was achieved by adding a suspension of cellulose powder (10 g) in 6*N* hydrochloric acid, instead of in water. When the cellulose had settled, a circle of filter paper was placed on top of the column, which was then washed with water, 0·2*N* sodium hydroxide solution and again water. It was essential to avoid prolonged contact of cellulose with 6*N* acid, which apparently caused slight degradation that led to cellulosic material being carried into the sodium hydroxide effluent and slowly precipitated in the re-acidified solution. If tungstophosphoric acid were determined in such a solution, the weight of precipitate obtained might be 2–3 mg too high. In practice, columns were recycled, when necessary, and equilibrated with 6*N* hydrochloric acid just before use. Tungstophosphoric acid was collected on and removed from columns without delay, a suitable flow-rate for solutions being 3–5 ml per min. The low solubility of

TABLE IV—DETERMINATION OF TUNGSTEN IN ASSOCIATION WITH 200 MG OF IRON

Phosphate (PO_4) present, *mg*	Tungsten taken, *mg*	Tungsten found, *mg*	Tungsten in first part of column effluent, *mg*
43	200·0	200·2	<0·2
17	200·0	200·2	<0·1
43	50·0	49·7	0·1
43	50·0	49·9	0·2

sodium chloride in 6*N* hydrochloric acid usually caused it to separate out. Warm solutions, applied to columns, deposited crystals within the pores of the upper disc of filter paper and clogged it. With cold solutions no clogging occurred.

Method for tungsten

To 200 or 50 mg of tungsten^{VI} in 20 ml of water 200 mg of iron^{III} (as sulphate), 0·7 ml of concentrated sulphuric acid and 6 ml of 12*N* sodium hydroxide solution were added. Phosphate was added to the hot stirred solution and then 12*N* hydrochloric acid quickly from a burette until hydrated iron^{III} oxide was dissolving. The solution was cooled, doubled in volume with 12*N* acid, recooled and applied to a column of cellulose in equilibrium with 6*N* acid. After the rejection of 30 ml of effluent the liquid was collected. In order to avoid having an excessive amount of acid afterwards in the tungstophosphate solution collected from the column, the latter was washed with 50 ml of 6*N* acid, then with 20 ml of water. Tungstophosphate was eluted by means of 30 ml of 0·2*N* sodium hydroxide solution and 30 ml of water. The solution was made strongly alkaline with 12*N* sodium hydroxide solution, 43 mg of phosphate were added, then sufficient 12*N* hydrochloric acid was run quickly dropwise into the hot stirred solution to give finally 100 ml of 1*N* acid. 100 Mg of ascorbic acid were added to the hot solution before precipitation of tris(tributylammonium) tungstophosphate, which was separated and weighed.

Behaviour of manganese, chromium, tin and tantalum plus niobium in the above procedure

When 200 mg of manganese^{II} were substituted for iron, some oxidation occurred in the alkaline solution. When the acidified solution was put on the column, a purple complex travelled slowly through the cellulose and 200 mg of tungsten yielded 0·3% to the first part of the effluent. The remaining tungsten was not determined since ascorbic acid would prevent the interference of accompanying manganese (p. 45).

Chromium^{III} could not be quantitatively separated from the heteropolyacid formed in its presence. Even 25 mg caused the loss of several mg of tungsten to the

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first fraction of column effluent and some chromium remained on the cellulose. Interference was prevented by forming chromate. Several drops of bromine and then an excess of sodium hydroxide solution were added to the solution containing tungstate and 25 mg of chromium^{III}, which was afterwards treated as usual. No tungsten escaped initially from the column and the recovery was almost complete.

25 Mg of tin^{IV} with 200 mg of tungsten^{VI} caused the loss of 0·9% of tungsten from the column and an apparent recovery of 99·5% with tributylamine. In the presence of tantalum^{V} and niobium^{V} together (5 mg of each) the corresponding values were 0·1% and 102·8%. (*cf.* p. 45). Obviously, very little of these elements could be tolerated.

DETERMINATION OF TUNGSTEN IN FERROTUNGSTEN, SCHEELITE AND WOLFRAMITE

At present the proposed method could be applied only to samples containing insignificant amounts of molybdenum, vanadium, titanium, tantalum and niobium

TABLE V—RESULTS FOR THE DETERMINATION OF TUNGSTEN

Sample	Tungsten found by new method, %	Tungsten found by classical methods, %
Ferrotungsten	81·9, 81·9	81·3*
Scheelite	44·3, 44·4	44·6, 44·9
Wolframite	59·1, 59·2	60·0, 59·9

* Certificate value

and small amounts of chromium and tin. British Chemical Standard ferrotungsten No. 242 (0·1% of tin) was used. Samples of scheelite and wolframite, kindly supplied by the late Dr. A. M. Cockburn of Edinburgh University, were analysed by classical procedures,[7] quantitatively for tungsten and semiquantitatively for elements commonly present that might interfere. The scheelite contained about 25% of silica, a little iron, an amount of tin that could be ignored, $\gtrsim$0·1% of tantalum and niobium, and no molybdenum or titanium. The wolframite contained iron and manganese, a little silica, a trace of molybdenum and about 0·1% of niobium.

It was, therefore, concluded that the new method for tungsten could be applied to all of these samples, the cellulose-column procedure being required only for ferrotungsten and wolframite.

Procedure for ferrotungsten

Use a 25-ml platinum crucible. To an amount of material containing $\gtrsim$200 mg of tungsten add 1 ml of hydrofluoric acid (40%) and 1 ml of concentrated sulphuric acid. Add 1 drop of concentrated nitric acid, heat gently, if necessary, to initiate reaction and cautiously add more nitric acid until disintegration is complete. Expel hydrofluoric and nitric acids by heating the crucible at a controlled temperature, in a metal block or on a hot-plate, and finally heat carefully with a micro Bunsen burner until sulphuric acid is fuming strongly. Allow to cool, transfer the contents of the crucible to a beaker with a minimum amount of water and four 1-ml rinsings, alternately with 2*N* sodium hydroxide solution and 2*N* hydrochloric acid. The volume at this stage should not exceed 25 ml. Next add 12*N* sodium hydroxide solution to the magnetically stirred solution until precipitation of hydroxides is complete and a 2-ml excess is present, heat the solution to about 80° and add 160 mg of hydrated

disodium hydrogen phosphate (43 mg of PO_4). Finally, while maintaining the heating, add 12*N* hydrochloric acid rapidly dropwise until hydrated iron^{III} oxide is just dissolving (pH ~ 1) and wait until solution is nearly complete. (It is permissible to increase the acidity of the hot solution to 1*N* to assist solution.) Cool the solution, raise the acid concentration to 6*N* by adding 12*N* acid and transfer it to a suitably prepared column (p. 48). Wash the beaker and column with 50 ml of 6*N* acid, then the column with 20 ml of water. Elute tungstophosphoric acid from the column with 30 ml of 0·2*N* sodium hydroxide solution and 30 ml of water.

Neutralise the eluate with 12*N* sodium hydroxide solution and add 2 ml more, then add phosphate and 12*N* hydrochloric acid to the hot solution as above until the pH is ~1. At this point increase the volume to 90 ml with water and the acid concentration to 1*N*, add 100 mg of ascorbic acid to the hot solution, and precipitate and separate the tributylammonium complex.

Procedure for minerals

To a sample containing up to 200 mg of tungsten add 3 ml of hydrofluoric acid and, after 15 min, 1 ml of nitric acid. Heat the containing crucible gently on a temperature-controlled hot-plate, then cool and cautiously add 1 ml of concentrated sulphuric acid. Thereafter, in analysing wolframite, follow the instructions given for ferrotungsten. With scheelite omit the column treatment and instead, after forming tungstophosphoric acid in the hot solution (pH 1), make 100 ml of 1*N* acid solution add ascorbic acid and precipitate tributylammonium tungstophosphate.

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Zusammenfassung—Die Überführung von Wolfram in Phosphorwolframsäure zur Bestimmung mit Tri-*n*-butylamine benötigt Ansäuern der alkalischen Lösung, die Wolfram und Phosphat enthält. Schwierigkeiten, die durch Anwesenheit von grösseren Mengen Eisen entstehen, werden vermieden, wenn man die Phosphorwolframsäure aus 6*N* Salzsäure an einer Kolonne von Cellulose adsorbiert. Die Kolonne hält Eisenchlorid nicht zurück. Die Bedingungen, unter denen die Heteropolysäure quantitativ zurückgehalten wird, sind kritisch. Nachdem das Adsorbat eluiert wurde, können kleine Mengen Eisen durch Reduktion unschädlich gemacht werden, bevor die Phosphorwolframsäure gefällt wird. Störungen durch einige andere Metalle wurden kurz studiert.

Résumé—La transformation du tungstène en acide 12-tungstophosphorique pour le dosage de la tri-*n*-butylamine nécessite l'acidification d'une solution alcaline contenant du tungstate et du phosphate. Des complications liées à la présence de grandes quantités de fer ont été résolues en faisant adsorber l'acide tungstophosphorique en solution acide chlorhydrique 6*N* sur une colonne de cellulose, qui n'adsorbe pas le chlorure ferrique. Les conditions de formation de l'hétéropolyacide qui conduisent à sa fixation quantitative sont critiques, et il semble qu'un peu de fer soit lié au tungstène. Quand le composé adsorbé a été extrait de la colonne, on peut rendre la faible quantité de fer qu'il contient inoffensive par réduction avant la précipitation du tris(tri-*n*-butylammonium)12-tungstophosphate. L'effet de différents autres éléments a été brièvement étudié.

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SHORT COMMUNICATION

Contributions to the basic problems of complexometry—IV
Determination of thallium

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For the complexometric determination of mono- and tervalent thallium, several methods have been proposed. Thallium^{III} can be reliably determined by direct titration with EDTA using Xylenol Orange[1] or PAN as indicator.[2] The indirect determination of thallium, which has also been proposed, depends on the back-titration of excess of EDTA with thorium nitrate[3] at pH 3·5 using Alizarin S. Flaschka[4] recommends the direct titration of thallium in an alkaline medium using Eriochrome Black T, after first adding Mg–EDTA complex. The conditions for the determination of thallium^{I} were studied by Foley and Pottie.[5] Titration in an ammoniacal medium was followed spectrophotometrically at 222 mμ.

Table I.—Determination of thallium in thallium^{I} iodide. Evaporation with nitric acid. The residue, after evaporation, diluted to 100 ml, pH adjusted to 3·0–3·2, and titrated with 0·01*M* or 0·05*M* EDTA, with Xylenol Orange as indicator.

Tl^{I} taken, *mg*	Tl^{I} found, %	Remarks
200·8	5·87	1 × (2 ml HNO_3 − 2 ml H_2O)
99·9	16·05	1 × (2 ml HNO_3 − 2 ml H_2O)
50·8	16·11	1 × (2 ml HNO_3 − 2 ml H_2O)
200·5	27·42	1 × 10 ml HNO_3
50·3	29·28	1 × 10 ml HNO_3
200·2	24·60	20 ml HNO_3 − 10 ml H_2O
50·9	82·94	20 ml HNO_3 − 10 ml H_2O
1·80	45·45	10 ml HNO_3
1·40	89·10	20 ml HNO_3
2·50	68·70	30 ml HNO_3
4·10	13·41	10 ml HNO_3
5·70	14·70	20 ml HNO_3
5·00	51·70	30 ml HNO_3

HNO_3 1:1

The complexity constants of Tl-EDTA complexes of both valencies have not yet been measured. From the analytical results, it is assumed that thallium^{III} forms a substantially stronger complex than that of lead, cadmium or zinc (pK_{Me} 16–18), because their presence does not interfere with the determination of thallium^{III} in a weakly acidic medium. Thallium^{I} which forms a relatively weak complex in an alkaline medium behaves quite differently. The existence of Tl^{I}–EDTA complex was proved[5] from the decrease and shift of polarographic waves. Further, thallium does not precipitate in an ammoniacal medium with iodide[6] (solubility product $2·8 \times 10^{-8}$). In an acidic medium, on the other hand, thallium^{I} in the presence of EDTA can be separated from many elements (Cu, Fe, Pb etc.) by precipitation with iodide, or it can be determined amperometrically.[7] From the experiments outlined, it can be reasoned that the stability constant should be of the same order as that of silver (pK 7–8).

Flaschka[4] in his early work on the determination of thallium, isolated thallium from an EDTA medium as iodide,[7] which he decomposed with nitric acid. In the solution obtained he presumed the

presence of thallium^{III}. Using the same procedure he prepared his stock solutions of thallium nitrate by decomposition of thallium iodide. This is not in agreement with the early literature according to which decomposition of thallium iodide with nitric acid yields thallium^{I} nitrate only. Flaschka's method had been evolved, of course, at a time when a suitable indicator for thallium^{III} was not known. Now, when Xylenol Orange has been found to be a very suitable indicator for thallium^{III}, we are able to control very easily the content of thallium^{III} in thallium solutions. As a result of many experiments it was proved that decomposition of thallium iodide by evaporation with concentrated nitric acid yielded thallium^{III} in small amounts only (Table I). With small weighed amounts of thallium iodide, thallium^{III} is mainly formed, but never quantitatively. With Flaschka's method, even after repeated experiments with monovalent or tervalent thallium, we never obtained a sharp colour change using Eriochrome Black T. Thallium iodide could be quantitatively transformed to thallium^{III} nitrate by a careful evaporation with *aqua regia* only. In Table II some results (including experimental conditions) are given of thallium determinations in thallium iodide after its decomposition in *aqua regia*. Oxidation of thallium ions with bromine water was found not to be advantageous, because the resulting bromide ions form very stable complexes with thallium^{III} which render this determination invalid. Oxidation with potassium permanganate was likewise unsuitable.

TABLE II.—DETERMINATION OF THALLIUM IN THALLIUM^{I} IODIDE. EVAPORATION WITH *AQUA REGIA*. Procedure as in Table I.

Tl^{I} taken, *mg*	Tl^{I} found, %	Remarks
200·6	99·53	2 ml *aqua regia* — 2 ml H_2O
50·8	98·57	2 ml *aqua regia* — 2 ml H_2O
200·1	99·61	5 ml *aqua regia*
51·4	99·04	5 ml *aqua regia*
200·1	99·85	20 ml *aqua regia* — 10 ml H_2O
100·0	99·98	20 ml *aqua regia* — 10 ml H_2O
50·1	100·20	20 ml *aqua regia* — 10 ml H_2O

From the theoretical point of view the sequential determination of tervalent and monovalent thallium in the same solution is extremely interesting. It would be the first complexometric determination of the element in both valency forms. As was said above, thallium^{III} could be reliably determined in the presence of thallium^{I} by direct titration with EDTA using Xylenol Orange in a weak acid medium (Table III). Subsequent titration of thallium^{I} in an alkaline medium, however,

TABLE III.—DETERMINATION OF THALLIUM^{III} IN THE PRESENCE OF THALLIUM^{I}. The mixture of $TlCl_3$ and TlCl was diluted to 100 ml, pH adjusted to 3·0–3·2 with monochloracetic acid and titrated with 0·05*M* EDTA with Xylenol Orange as indicator.

Tl^{3+} taken, *mg*	Tl^{+} taken, *mg*	Tl^{3+} found, *mg*	Difference, *mg*
9·99	60·80	10·06	+0·07
30·25	60·80	30·35	+0·10
50·48	60·80	50·69	+0·21
201·90	60·80	202·29	+0·39
9·99	101·38	10·17	+0·18
9·99	404·70	10·06	+0·07

fails. The oxidation of thallium^{I} to thallium^{III} with potassium bromate, and its titration with EDTA following titration of the thallium^{III}, also fails (see the note on oxidation with bromine). The mixture of tervalent and monovalent thallium may, however, be analysed in the following way: In one aliquot of the solution thallium^{III} is determined by direct titration with EDTA using Xylenol Orange. In a

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second aliquot of the solution the thallium^{I} is determined by potentiometric titration with potassium bromate. Another procedure depends on evaporation of the sample with *aqua regia* and on the complexometric determination of total thallium.

It has to be emphasised that all titrimetric methods for the determination of thallium are unfavourably influenced by the high atomic or equivalent weight of the element.

The results of the study of selective determination of thallium will be published later.

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Summary—It has been shown that Thallium^{I} iodide, by evaporation with nitric acid, forms mainly Thallium^{I} nitrate and not Thallium^{III} nitrate, as assumed in the recent literature[4]. Only decomposition with *aqua regia* leads to the quantitative formation of Thallium^{III} nitrate. It has further been found that titrations of Thallium^{I} and Thallium^{III}, in alkaline medium using Eriochrome Black T, do not give reliable results, since the colour change with this indicator is not sharp enough. The titration with Xylenol Orange, in acid medium, is, however, quite reliable, and permits the determination of Thallium^{III} in the presence of Thallium.^{I}

Zusammenfassung—Es wurde gezeigt, dass Thallium(I)jodid, wenn mit Salpetersäure abgeraucht, in der Hauptsache Thallium (I)nitrat und nicht Thallium(III)nitrat gibt, entgegen den Annahmen jüngster Literatur. Nur Abrauchen mit Königswasser führt zur quantitativen Bildung von Thallium (III)nitrat. Es wurde weiterhin gefunden, dass die Titration von Thallium(I) und Thallium(III) in alkalischem Medium mit Eriochromschwarz T als indicator unzuverlässige Resultate ergibt, da der Farbwechsel dieses Indicators nicht genügend scharf ist. Die Titration mit Xylenolorange in saurem Medium ist jedoch zuverlässig und gestattet die Bestimmung von Thallium(III) in Gegenwart von Thallium(I).

Résumé—Les auteurs ont montré que, per évaporation avec l'acide nitrique, l'iodure de thallium (I) forme surtout du nitrate de thallium (I) et non du nitrate de thallium (III), comme cela était supposé dans la littérature récente. Seule la décomposition avec l'eau régale conduit à la formation quantitative de nitrate de thallium (III). On a trouvé ultérieurement que la titrage du thallium (I) et du thallium (III), en milieu alcalin, en utilisant le noir ériochrome T, ne donne pas de résultats sûrs, car le changement de couleur avec cet indicateur n'est pas assez net. Le titrage avec le xylénol orange, en milieu acide, est cependant, tout à fait sûr, et permet le dosage de thallium (III) en présence de thallium (I).

REFERENCES

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[2] A. I. Busev and V. G. Tipcova, *Zhur. analit. Khim*, 1958, **13**, 180.
[3] W. T. Foley and R. F. Pottie, *Analyt. Chem.*, 1956, **28**, 1101.
[4] H. Flaschka, *Mikrochem.*, 1952, **40**, 42.
[5] R. Přibil and Z. Zábranský, *Chem. Listy*, 1951, **45**, 427.; *Coll. Czech. Chem. Comm.*, 1951, **16**, 554.
[6] R. Přibil, *Chem. Listy*, 1951, **45**, 57; *Coll. Czech. Chem. Comm.*, 1951, **16**, 542; *Magyar Kém. Folyóirat*, 1952, **58**, 251.
[7] R. Přibil and Z. Zábranský, *Chem. Listy*, 1952, **46**, 16.

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NOTICE

The following meetings have been arranged:

Wednesday 1 *February* 1961: **Society for Analytical Chemistry:** *X-ray fluorescence.* Burlington House, London, W.1. 7.00 p.m.

Wednesday 15 *February* 1961: **Society for Analytical Chemistry,** Biological Methods Group: *Use of enzymes in biological assay.* Burlington House, London, W.1. 7.00 p.m.

Thursday 16 *February* 1961: **Society for Analytical Chemistry,** Midlands Section and **Association of Clinical Biochemists:** *Chromatography:* Mr. N. F. KEMBER, A.R.I.C. and Dr. H. G. SAMMONS. General Hospital, Birmingham, 6.30 p.m.

Thursday 23 *February* 1961: **Society for Analytical Chemistry,** Western Section and **Royal Institute of Chemistry,** Bristol and District Section: *Titrations in non-aqueous solvents:* MR. E. MINSHALL, M.Sc., F.R.I.C. Gloucester.

Friday 24 *February* 1961: **Society for Analytical Chemistry,** Scottish Section and **Royal Institute of Chemistry:** Joint Meeting: *Ion-exchange*: Mr. R. A. WELLS, B.Sc., A.R.I.C. and Mr. V. E. GRIPP, B.Sc., A.R.C.S., A.R.I.C. Royal College of Science and Technology, Glasgow C.1.

Friday 24 *February* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Annual General Meeting followed by Retiring Chairman's Address: Mr. F. HOLMES, B.Sc., A.R.I.C. Burlington House, London, W.1. 7.00 p.m.

Tuesday 28 *February* 1961: **Society for Analytical Chemistry,** Physical Methods Group: *Physical methods of analysis in medical research.* Royal College of Surgeons, London, 6.30 p.m. Preceded by a visit to the Research Department of Anaesthetics.

B.S.I. News announces the following new British Standards:

B.S. 1792: *One-mark volumetric flasks:* 1960. This specifies ten sizes of flask, from 5-ml to 2000-ml capacity. It gives full dimensions but, in accordance with current practice in British Standards for volumetric glassware, lists only the essential ones as mandatory, the remainder being given for the guidance of manufacturers. It includes a standard method for the determination of capacity and lists two classes of tolerance for this. It specifies requirements for material, construction, stability and graduation, and includes alternative shapes of neck suitable for stoppers of ground glass or plastics materials. (Price 4s.)

B.S. 3266: *Methods for the determination of conductivity, pH, water-soluble matter, chloride and sulphate in aqueous extracts of textile materials:* 1960. This specifies associated test methods and includes two standardised procedures for extracting textile specimens with water. Methods for determining conductivity, pH value, water-soluble matter, chloride and sulphate content of the aqueous extracts are included. (Price 4s.)

B.S. 3278: *General recommendations for the sampling of imported iron ores: Part I:* 1960: *Hammer and shovel method.* These recommendations apply to the sampling of imported iron ores from ship's holds at the port of arrival immediately after arrival. Recommendations are made for the method of selection of the sub-samples and the number of increments, the method of sampling, the gross sample and the reduction of the certificated sample, and the final samples. A plan of sampling. and sampling reduction is included, as well as an appendix giving an example of the general procedure recommended. (Price 3s.)

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PAPERS RECEIVED

Gravimetric and titrimetric determination of bismuth using ammonium salts of benzene- and naphthalene-selenoyl acids: V. S. SOTNIKOV and I. P. ALIMARIN (27 *September* 1960).

Determination and separation of scandium using *N*-benzoylphenylhydroxylamine: I. P. ALIMARIN and TZE YUN'-SYAN (27 *September* 1960).

A laboratory method for the purification of commercial niobium and tantalum oxides: EDWARD C. MURRAY (14 *October* 1960).

Isotope dilution analysis by solvent extraction—I: Principle and theory of the method: JAROMIR RUZICKA and JIRI STARY (15 *October* 1960).

Isotope dilution analysis by solvent extraction—II: Highly selective determination of zinc with dithizone: JIRI STARY and JAROMIR RUZICKA (15 *October* 1960).

Analytical applications of Xylenol Orange—VI. The photometric determination of zinc: KAREL STUDLAR and IVAN JANOUSEK (16 *October* 1960).

Spectrophotometric determination of germanium with *p*-dimethylaminophenylfluorone: A. CAMPE and J. HOSTE (17 *October* 1960).

Activation-analysis of manganese in cast iron and high-alloy steels: P. BOUTEN and J. HOSTE (17 *October* 1960).

The determination of traces of iridium in samples of rhodium by neutron-activation and gamma-ray spectrometry: D. F. C. MORRIS, D. N. SLATER and R. A. KILLICK (17 *October* 1960).

The separation of sub-microgram amounts of uranium from milligram amounts of iron, aluminium and plutonium: D. G. BOASE and J. K. FOREMAN (17 *October* 1960).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution, III. Aluminium: DAVID J. MAREC, EUGENE D. SALESIN and LOUIS GORDON (18 *October* 1960).

Spectrophotometric determination of palladium with nitroso-R salt: JACOB SHAMIR and ABRAHAM SCHWARTZ (19 *October* 1960).

The selective determination of active hydrogen with dispersed sodium: PATRICIA R. MOHILNER and CHARLES A. REYNOLDS (21 *October* 1960).

Separation and colorimetric determination of trace quantities of magnesium in high-purity beryllium oxide: R. F. APPLE and J. C. WHITE (24 *October* 1960).

A critical examination of the gravimetric and titrimetric methods for the determination of gold: F. E. BEAMISH (26 *October* 1960).

The analysis of beryllium and beryllium oxide—VI: The determination of tantalum and niobium: JAMES O. HIBBITS, H. OBERTHIN, R. LIU and SILVE KALLMANN (27 *October* 1960).

The determination of oxygen, hydrogen, nitrogen and carbon in metals: A review: WILLIAM G. GULDNER (1 *November* 1960).

New methods of inorganic ultramicroanalysis under the microscope: I. P. ALIMARIN, and M. N. PETRIKOVA (6 *November* 1960).

Determination of calcium in lithium salts: RODNEY L. OLSEN, HARVEY DIEHL, PETER F. COLLINS and R. B. ELLESTAD (10 *November* 1960).

Applications of complementary tri-stimulus colorimetry—IV: Investigation of a tartrate complex containing both copper and aluminium: H. FLASCHKA, J. BUTCHER and R. SPREIGHTS (10 *November* 1960).

The precipitation of niobium oxinate of definite composition: L. KOSTA and R. DULAR (13 *November* 1960).

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THE MICRO-KJELDAHL DETERMINATION OF NITROGEN

AN INVESTIGATION OF THE EFFECTS OF ADDED SALT AND CATALYSTS

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Summary—An examination has been made of the effects of concentration of potassium sulphate and of 21 single and mixed catalysts on the recovery of nitrogen by the Kjeldahl method. Mercury has been confirmed as the best catalyst, and a higher concentration of potassium sulphate than usual is recommended. Observations are made on various factors, including the "clearing time", which affect the determination.

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INTRODUCTION

IN spite of the widespread use of the Kjeldahl method for the determination of nitrogen, no one has yet undertaken a comprehensive comparison of a number of catalysts under varying conditions. Previous investigators have either investigated different catalysts under one set of conditions only, or have varied the conditions, but with only one or two catalysts. In many cases the test substances used have been simple amino compounds, which would not be expected to give any difficulty, whatever modification was used. In some cases, non-nitrogenous test substances were used to investigate "clearing times", but no attempt was made to demonstrate that the proposed conditions would lead to quantitative recovery of nitrogen from a nitrogenous sample.

In the present work, the behaviour of different catalysts at varying salt concentrations has been investigated. The boiling points of solutions of varying concentrations of added salt have also been determined.

THE INFLUENCE OF TEMPERATURE ON THE DIGESTION

The addition of potassium sulphate was first suggested by Gunning,[1] who recommended the use of "one part of salt to two parts of acid", *i.e.* 0·9 g of salt to 1·0 ml of acid. Later, Hibbard[2] and Self[3] found that a loss of ammonia could occur if the salt concentration became excessive, but many workers apparently did not appreciate that the excessive concentrations referred to involved about 2 to 3 g of potassium sulphate to 1 ml of sulphuric acid, and in consequence used absurdly small concentrations of salt; as low as 0·1g to 1ml of acid. In fact, recent work[4,5] has shown that as much as 1·0 g of salt to 1·0 ml of acid may safely be used.

Gunning thought that the addition of potassium sulphate, giving potassium hydrogen sulphate in solution, would lead to the loss of water rather than sulphur trioxide on heating, and hence a stronger acid would be formed, which would speed the digestion of the sample. Whether or not this is true, it is generally agreed nowadays that the primary function of the salt is to raise the boiling point of the mixture (which will have the same effect of speeding the digestion).

Only six previous investigations have been made of the boiling points at varying salt concentrations, and only one of these has gone above 1·0 g/ml concentration. This work is summarised in Table I (in some cases, the figures given have been estimated from the original author's graph).

These results, and possible reasons for the discrepancies, will be discussed later, in conjunction with the results of the present investigation.

TABLE I—BOILING POINTS (°C) OF SOLUTIONS OF POTASSIUM SULPHATE IN SULPHURIC ACID

Concn. of K_2SO_4, *g/ml*	Snyder and Coleman[6]	Ogg and Willits[7]	Middleton and Stuckey[8]	Lake *et al.*[9]	McKenzie and Wallace[5]	Bradstreet[10]
0	345	—	328	—	—	322*
0·25	350	332	336	—	—	329
0·33	—	—	339	—	344	333
0·5	356	342	347	362	—	339
0·67	—	—	—	367	361	346
0·75	372	354	359	371	—	349
1·00	—	—	371	382	380	—
1·33	—	—	—	—	397	—
1·67	—	—	—	—	418	—
2·00	—	—	—	—	406†	—

* at 0·08 g/ml
† This value is probably erroneous[11]

EXPERIMENTAL

The present measurements were carried out using a thermometer (in about 10 ml of solution) and a small copper-constantan thermocouple (in about 1·5 ml of solution).

Use of a thermometer

A 0–500° mercury thermometer was used. Calibration with naphthalene and benzophenone (recommended[12] as secondary fixed points) showed that it was accurate at 218° and 2° low at 306°. For the present purpose it was considered sufficient to apply a 2° correction to readings between 300° and 400°. Determinations were then carried out on boiling solutions of potassium sulphate in sulphuric acid, contained in a "30-ml" Kjeldahl flask. In each case the bulb of the thermometer was immersed in the liquid, and about 6 in. of stem were in the vapour. The solutions were boiled vigorously so that acid just distilled from the neck of the flask, and the maximum steady boiling point was noted. The results obtained are shown in Table II.

TABLE II—BOILING POINTS OBTAINED WITH THERMOMETER

K_2SO_4, *g*	H_2SO_4, *ml*	Concentration, *g/ml*	Corrected b.p., °C
0	10	0	329
5	10	0·5	344
7	7	1·0	365
9	6	1·5	388
10	5	2·0	410

Use of a thermocouple

This was made from fine wires, and enclosed in a thin glass sheath. It was calibrated at seven points up to 400° in the following manner.

At the ice point both the hot and cold junctions were immersed in a beaker of melting ice and the millivoltmeter adjusted to zero. Measurements were then taken at the boiling points of water, bromobenzene, naphthalene, diphenyl and benzophenone, and at the melting point of potassium dichromate, using for this last point a furnace similar to that recommended.[12]

From these figures a calibration curve was obtained which was slightly curved between 0 and 200° but linear from 200–400°.

Using this calibration, the boiling point of 10 ml of sulphuric acid was found to be 330°. When only 1·5 ml was used, the boiling point was less stable, and fluctuated between 328° and 330°. For subsequent work, using 1·5 ml of acid, 30-ml Kjeldahl flasks and a gas-heated rack were used. In each determination the mixture of acid and salt was heated gently over a low gas flame for 2 or 3 min to dissolve most of the solid, then the flame was increased.

The results obtained are shown in Table III.

TABLE III—BOILING POINTS OBTAINED WITH THERMOCOUPLE

Expt.	H_2SO_4, *ml*	K_2SO_4, *g*	Conc., *g/ml*	B.p., °C	Remarks
1	1·5	—	—	329	
2	1·5	0·75	0·5	344 ± 1	Maximum value attained in 5 min from start of ebullition. Constant for further 15 min.
3	1·5	1·5	1·0	364 ± 2	Attained in 8 min. Slight overall rise (362–365°) during succeeding 20 min.
4	1·5	2·25	1·5	387	Steady for 10 min.
5	1·5	3·0	2·0	404	Attained in 9 min, rising to 407° during further 25 min.
6	Solid $KHSO_4$		[= 3·3]	—	Evolution of bubbles at *ca.* 320°; steady temperature rise to >415°. No steady boiling point.

Although, as shown in Table III, the rise in temperature during digestion for about 20 min was not serious, it was thought desirable to find directly, by titration, if there was a significant loss of acid. Accordingly, the residual solutions from experiments 1, 3 and 5 in Table III were diluted to 500 ml, and aliquots titrated against 0·1*N* sodium hydroxide. The results were as follows:

Solution 1 contained 2·69 g of sulphuric acid
Solution 3 contained 2·70 g of sulphuric acid
Solution 5 contained 2·70 g of sulphuric acid
1·5 ml of sulphuric acid, not boiled, contained 2·74 g (theoretical = 2·71 g).

The discrepancy between the theoretical and observed values is probably due to inaccuracies in pipetting such a viscous liquid. Nevertheless, the apparent loss of acid on digestion (0·04 g) would only be sufficient to raise the boiling point by less than 1°, and consequently the loss of acid by evaporation is negligible under these conditions.

The boiling points obtained by the two methods, shown in Table IV, are thus in satisfactory agreement.

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TABLE IV.—RESULTS OBTAINED BY THE TWO METHODS

K_2SO_4 concentration, *g/ml*	0	0·5	1·0	1·5	2·0
B.p. with thermometer, °*C*	329	344	365	388	410
B.p. with thermocouple, °*C*	329	344	364	387	405

DISCUSSION OF RESULTS

There is a considerable discrepancy in the literature over the boiling point of sulphuric acid alone. The approximately 98·4% acid is a constant boiling mixture, usually said to boil between 328–330°, but textbook values as far apart as 317°[13] and 338°[14] have been found. Recently, however, Kunzler,[15] in connection with the preparation of pure sulphuric acid, has stated that the boiling point of constant boiling acid (98·5%) is "nearly 330° at one atmosphere", and this figure has been confirmed in the present work. Neither Snyder and Coleman[6] nor Bradstreet,[10] however, whose results are quoted in Table I, commented on their figures of 345° and less than 322° respectively.

The figures of Lake *et al.*[9] appear somewhat high, but their values were recorded after boiling for 1 hr, during which time considerable evaporation could have occurred. They do not give a figure for sulphuric acid alone.

Our figures are in agreement with those of Ogg and Willits,[7] and Middleton and Stuckey,[8] but those of McKenzie and Wallace,[5] the only other workers to report comparable figures, are somewhat higher. Moreover, a graph of boiling point against concentration for their results shows a steeper slope than for those of other workers. Two reasons can be advanced for this. McKenzie[11] has stated that the intensity of heating used by him was greater than that used by us, which would lead to more rapid evaporation of acid, and hence a higher temperature. This effect would increase with increasing concentration. The second reason, apparently hitherto overlooked, is related to the amount of acid in the vapour phase, and distributed round the walls of the vessel. If the mixture is barely boiling, there will be very little acid in the vapour phase, and the concentration of the mixture will approximate to that calculated, but if boiling is vigorous, the amount of acid in the vapour phase will be greater, the interior of the vessel will be covered with a film of condensing acid, and the boiling solution at the bottom of the flask will, in consequence, be more concentrated. The effect will of course be more marked when "micro" quantities are used.

The effect on the boiling point of other substances present during digestion

The consumption of acid during digestion of an organic sample is greatest for fat, and is then about 10 ml of acid for 1 g of sample, or 0·05 ml for 5 mg. (Middleton and Stuckey[8] give the acid consumption for a number of compounds and molecular fragments). Using 1·5 ml of acid, a 5-mg sample would have the effect of raising an initial salt concentration of 1·0 g/ml to 1·035 g/ml which would raise the temperature by only about 1·5°.

Similarly, the presence of about 50 mg of catalyst would raise the boiling point only to a similar extent, and hence these factors may be ignored on the micro-scale.

The effect on the boiling point of variations in atmospheric pressure

The work of Lake *et al.*[9] indicates that the boiling point changes by about 15° for a pressure change of 175 mm of Hg. Variations in normal atmospheric pressure (740–770 mm) will therefore affect the boiling point by not more than 2–3°.

The effect of replacing potassium sulphate by sodium sulphate

Sodium sulphate, having a smaller molecular weight, might be expected to give a greater boiling point elevation than potassium sulphate, but the contrary has been reported,[5,8] and this unexpected finding has been confirmed in the present work. At a concentration of 1·0 g/ml, a solution of sodium sulphate gave a boiling point 7° lower than that of potassium sulphate.

THE INFLUENCE OF DIFFERENT CATALYSTS ON THE DIGESTION

The use of catalysts was first suggested by Wilfarth.[16] He investigated mercury, copper, iron, tin, manganese, bismuth and lead, and found their relative efficiency to be in the order shown. Mercury, however, led to difficulty at the distillation stage, because of formation of non-volatile ammines, and he therefore preferred to use copper, but later in the same year,[17] he showed how the ammines could very easily be broken down by the addition of potassium sulphide.

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Subsequent work has confirmed the superiority of mercury (Phelps and Daudt[18] found it to be superior to 9 other elements, and Osborn and Wilkie[19] found it to be superior to 38 other elements) and it is therefore surprising that many analysts still prefer to use copper.

The only other single catalyst to gain widespread popularity is selenium, proposed by Lauro.[20] There has, however, been considerable controversy about the possible loss of ammonia when using this catalyst. Mixtures are frequently used; the most popular is a mixture of mercury and selenium, first suggested by Beet,[21] although here again a loss of ammonia has been alleged under certain conditions.

In the present work, the effects studied were (*a*) variation in the catalyst (15 single catalysts and 6 mixtures were used), (*b*) variation in the potassium sulphate concentration, and (*c*) variation in the type of sample (ammonium sulphate, benzylisothiouronium chloride, and nicotinic acid were used, typifying a simple ammonium salt, an easily digested compound, and a "refractory" compound).

The effect of variation in time was not studied, and a standard digestion time of 20 min was adopted. By comparing the results obtained with the three test samples, it could easily be seen whether the low results obtained under certain conditions were due to incomplete digestion or to decomposition of ammonia.

The effect of variation in the amount of each catalyst was not studied (the effect of a true catalyst should be independent of the amount, but this is probably not true in the present case). It was originally intended to use 0·2 mg mol of each catalyst (*e.g.* about 40 mg of HgO or 20 mg of Se, as commonly used), but it was soon apparent that this would lead to inconsistencies, and with the exception of a few of the early experiments, approximately equal amounts (20–30 mg) of each catalyst were used.

EXPERIMENTAL

Reagents

Sulphuric acid: Concentrated M.A.R.
Potassium sulphate: M.A.R.

Catalysts: The substances used were HgO, Se, H_2SeO_3, H_2SeO_4, $CuSO_4$, TiO_2, $FeCl_3$, $FeSO_4$, $Fe_2(SO_4)_3$, H_2PtCl_6, MoO_3, V_2O_5, $VOSO_4$, CrO_3, and Te. The best available commercial grade of each was used.

Ammonium sulphate: AnalaR.

Alkaline thiosulphate: 40% NaOH (w/v), containing 5% w/v $Na_2S_2O_3$.

Boric acid: AnalaR, 2% w/v in boiled-out distilled water.

Screened indicator: 2 vol. of 0·05% ethanolic methyl red + 1 vol. of 0·05% ethanolic methylene blue. (This has been found[22] to be superior to any other mixture of these components.)

Hydrochloric acid: standard 0·01*N* solution.

Procedure

About 5 mg of the test substance was weighed into a 30-ml Kjeldahl flask. The required weights of catalyst and potassium sulphate were added, followed by 1·5 ml of sulphuric acid. Each batch consisted of 5 such samples and one blank (containing sulphuric acid and potassium sulphate only). The 6 flasks were heated gently for 2–3 min, to dissolve most of the salt, then at full heat for 20 min.

After digestion, the flasks were allowed to cool. The contents were diluted with about 10 ml of water, and gently warmed if necessary to dissolve the "cake" of potassium hydrogen sulphate.

The contents of each flask, in turn, were then transferred to a distillation apparatus, and 10 ml of alkaline thiosulphate added (the addition of thiosulphate to the alkali is necessary only if mercury is used as a catalyst, but to avoid variation it was used throughout). The ammonia was then steam-distilled into 5 ml of boric acid, containing 4 drops of screened indicator. Distillation was allowed to proceed, at 4–5 ml/min, for 3 min with the tip of the condenser immersed in the boric acid, and a further 1 min with the tip clear of the surface. The end of the condenser was then washed down with water, and the contents of the receiver titrated against standard 0·01*N* hydrochloric acid.

DISCUSSION OF RESULTS

The results obtained are shown in Tables V–VII. Since several of the catalysts used affect both the rate of digestion and the loss of ammonia, it is more convenient to consider these two effects together. The question of the "clearing time" will be considered separately.

Using no catalyst, the recovery from ammonium sulphate was quantitative up to 440°, but the result of 17·6% obtained after a 20-min digestion with a mixture equivalent to potassium hydrogen sulphate shows that there is no "instantaneous" loss of ammonia at this salt concentration.

The results with benzylisothiouronium chloride were similar, and it thus appears that the maximum safe digestion temperature, using no catalyst, is about 430°. At this temperature, however, digestion of nicotinic acid was not quite complete.

Single catalysts

Mercury This catalyst had no apparent effect on the decomposition of ammonia, but a marked effect on the digestion of nicotinic acid, the recovery from which was satisfactory above 387°.

Selenium Elementary selenium caused decomposition of ammonia above about 387°. The recoveries from nicotinic acid were unsatisfactory, and hence selenium appears inferior to mercury in both these respects.

Experiments with selenious and selenic acids (*cf.* ref. 23) showed that the decomposition of ammonia was moderate with selenious acid, but very great with selenic acid. This effect, however, was not obvious with nicotinic acid, and it is likely that the reduction of selenate to selenite takes place more quickly than the digestion of nicotinic acid.

TABLE V—NITROGEN FOUND IN AMMONIUM SULPHATE
(Theoretical = 21·2% N)

K_2SO_4 concentration, *g/ml*		0	0·5	1·0	1·5	2·0	2·25	2·5	2·75	3·0	3·3
Temperature (from Table IV), °C		329	344	365	387	408	420*	430*	440*	450*	
Catalyst	Amount, *mg*										
None	—	—	—	—	—	21·3	—	20·9	21·3	16·8 18·0	17·6
HgO	40	—	—	—	21·2	21·3	—	21·2	21·2	19·0 12·8	—
Se	20	—	—	21·1	21·4	20·5	—	17·7	—	—	—
H_2SeO_3	25	—	—	21·3	20·9	19·3	—	—	—	—	—
H_2SeO_4	30	20·5	18·8	4·5	—	1·6	—	—	—	—	—
$CuSO_4$	75	—	—	—	—	21·1	19·6	18·7	—	—	—
TiO_2	20	—	—	—	—	21·3	—	20·7	—	—	—
$FeCl_3$	30	—	—	—	—	21·1	—	20·6	—	—	—
$FeSO_4$	30	—	—	—	—	21·2	—	20·5	—	—	—
$Fe_2(SO_4)_3$	30	—	—	—	—	21·2	—	—	—	—	—
H_2PtCl_6	80	—	—	nil	—	—	—	—	—	—	—
MoO_3	30	—	—	21·4	20·8	20·0	—	20·0	—	—	—
V_2O_5	20	20·8	20·3	19·0	18·2	15·2	—	—	—	—	—
$VOSO_4$	30	—	—	21·1	—	19·3	—	—	—	—	—
CrO_3	20	—	—	10·7	—	9·5	—	—	—	—	—
Te	25	—	—	—	—	21·1	—	19·9	—	—	—
HgO + Se	40/20	—	—	21·1	20·0	12·5	—	—	—	—	—
HgO + $CuSO_4$	40/20	—	—	—	21·3	20·9	—	20·8	—	—	—
Se + $CuSO_4$	20/20	—	—	—	21·2	20·5	—	—	—	—	—
HgO + Se + $CuSO_4$	40/20/20	—	—	21·0	19·7	17·7	—	—	—	—	—
V_2O_5 + Se	20/20	—	—	21·3	21·2	20·1	—	15·8	—	—	—
HgO + Te	40/20	—	—	—	21·2	21·0	—	20·6	—	—	—

* Extrapolated from a graph of the figures in Table IV

Copper This led to a loss of ammonia above 408°, and the recoveries from nicotinic acid were unsatisfactory.

Titanium This has never been recommended for routine use, but was briefly investigated in view of its high placing (fourth) in the list of Osborn and Wilkie.[19] It was found that loss of ammonia only occurred above 408°, and recovery of nitrogen from nicotinic acid was satisfactory only at this temperature.

Iron In view of somewhat conflicting statements in the literature iron was investigated as iron^{III} sulphate, iron^{III} chloride and iron^{II} sulphate. The mixture containing iron^{III} sulphate gave a cloudy suspension at once; that with iron^{III} chloride went cloudy almost at once, and that with iron^{II} sulphate gave an initially clear solution, which rapidly turned yellow, then cloudy, presumably due to oxidation followed by crystallisation of iron^{III} sulphate. The appearance at this stage was the same in all three cases; namely, a white precipitate in a yellow solution (the colour was discharged on cooling). It is apparent that, contrary to Stubblefield and De

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TABLE VI—NITROGEN FOUND IN BENZYLISOTHIOURONIUM CHLORIDE
(Theoretical = 13·8% N)

K_2SO_4 concentration, *g/ml*	1·0	1·5	2·0	2·5	3·0
Temperature (from Table IV), °C	365	387	408	430*	450*
Catalyst					
None	—	—	13·8	14·0	13·5
HgO	—	—	13·9	13·4	13·6
Se	—	13·9	12·4	—	—
H_2SeO_3	—	13·6	13·1	—	—
H_2SeO_4	—	6·9	—	—	—
$CuSO_4$	—	—	13·8	13·4	—
TiO_2	—	—	14·0	—	—
$FeSO_4$	—	—	14·0	13·7	—
$Fe_2(SO_4)_3$	—	—	13·7	13·5	—
MoO_3	—	—	13·4	—	—
V_2O_5	—	13·9	13·0	13·2	—
$VOSO_4$	—	13·8	13·3	13·2	—
Te	—	—	13·8	13·6	—
HgO + Se	13·7	13·7	9·1	—	—
HgO + $CuSO_4$	—	13·9	13·8	—	—
Se + $CuSO_4$	13·7	13·5	11·4	—	—
HgO + Se + $CuSO_4$	13·8	11·3	7·3	—	—
V_2O_5 + Se	—	—	13·6	6·8	—
HgO + Te	—	—	13·7	13·2	—

* See footnote to Table V

Turk,[24] iron^{III} sulphate is not completely insoluble in boiling sulphuric acid. Bradstreet,[25] who recommended the use of iron^{II} sulphate did not comment on the precipitation of iron^{III} sulphate. The precipitate did appear to make boiling more regular.

As anticipated from these observations, the results were substantially the same for all three compounds. Loss of ammonia was evident above 408°, and recovery from nicotinic acid was quantitative only at this temperature.

Platinum This was claimed to be a satisfactory catalyst by Ulsch,[26] but later work[19] indicated a considerable loss of ammonia. In the present work one experiment led to complete loss of ammonia, and it was not further investigated.

Molybdenum, Vanadium, and Chromium The use of molybdenum or vanadium both led to loss of ammonia, vanadium pentoxide being worse than vanadyl sulphate in this respect. No great catalytic activity was apparent, and it is likely that the oxides are oxidants rather than catalysts. To support this view, chromium trioxide was briefly investigated. This led to considerable loss of ammonia.

Tellurium This has been claimed[27] to be less efficient than selenium, but not to cause loss of ammonia, and this is borne out by the present results.

Mixed catalysts

Mercury and selenium This mixture causes decomposition of ammonia at a lower temperature than either component alone. The maximum recovery of nitrogen

TABLE VII—NITROGEN FOUND IN NICOTINIC ACID
(Theoretical = 11·4% N)

K_2SO_4 concentration, *g/ml*	1·0	1·5	2·0	2·5
Temperature (from Table IV), °C	365	387	408	430*
Catalyst				
None	2·2	—	7·1	10·9
HgO	10·6	11·3	11·2	11·1
Se	8·6	9·0	10·9	9·1
H_2SeO_3	6·3	10·6	10·5	10·1
H_2SeO_4	9·0	10·6	10·9	6·6
$CuSO_4$	8·9	—	9·3	—
TiO_2	6·8	—	11·3	—
$FeSO_4$	3·1	—	11·3	—
MoO_3	4·5	—	—	—
V_2O_5	7·5	—	—	—
$VOSO_4$	4·1	—	—	—
Te	3·5	8·8	10·6	—
HgO + Se	11·1	10·6	6·0	—
HgO + Cu	10·1	—	—	—
Se + $CuSO_4$	7·5	—	—	—
HgO + Se + $CuSO_4$	11·0	—	—	—
V_2O_5 + Se	10·4	10·8	9·9	—
HgO + Te	10·8	11·3	11·2	10·9

* See footnote to Table V

from nicotinic acid occurs at a lower temperature, but if this temperature is exceeded decomposition of ammonia again occurs.

Mercury and copper Paul and Berry[28] concluded that this mixture is not more effective than mercury alone and the present work supports this conclusion.

Selenium and copper; mercury and selenium and copper These mixtures behaved similarly to selenium, and mercury and selenium respectively. In the light of the results with mercury and copper this is not unexpected. It is significant that none of the workers[29–31] who have recommended the ternary mixture have given good evidence of its superiority. Poe and Nalder[30] claimed it to be better than mercury or copper alone, but did not compare it with a mixture of mercury and selenium, and in any case, only analysed simple amino compounds.

Vanadium and selenium This mixture, originally recommended by Crossley,[32] led to a loss of ammonia above 387°. The recoveries from nicotinic acid were higher than with either component alone but still not satisfactory.

Mercury and tellurium As tellurium alone was shown to cause no significant loss of ammonia it was hoped that this mixture might prove an attractive substitute for mercury and selenium. The results show that this is the case, but there is no apparent improvement over the use of mercury alone. Since, however, the "clearing times" for the mixture were somewhat shorter than for mercury alone, it was thought desirable to compare these two catalysts more closely, by determination of the rate of digestion of nicotinic acid, using 1·5 ml of sulphuric acid and 2·25 g of potassium sulphate. The results, in Table VIII, show no significant difference.

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TABLE VIII—COMPARISON OF MERCURY AND MERCURY-TELLURIUM CATALYSTS WITH RESPECT TO THE DIGESTION OF NICOTINIC ACID

Digestion time, *min*	Catalyst	
	Hg	Hg + Te
5	4·0%N	3·1%N
10	9·4	9·1
15	11·3	11·3
20	11·3	11·4

Amount of catalyst

A series of digestions of nicotinic acid was carried out, using 1·5 ml of sulphuric acid and 2·25 g of potassium sulphate, to determine the minimum amount of catalyst necessary. The results in Table IX show that 10 mg is adequate, and the use of 20 mg should provide an adequate margin of safety.

CONCLUSIONS

The results show clearly that none of the catalysts investigated is demonstrably superior to mercury, used alone, and it appears that there is no longer any justification for the use of any of the other catalysts mentioned.

THE "CLEARING TIME"

This, the time taken for the digest to become clear, has been widely used as a measure of the efficiency of the procedure. Clearing will obviously occur when all of the charred organic matter has been completely oxidised, but it does not necessarily follow that the conversion of nitrogen to ammonia will take place concurrently. Ashton,[33] for example, stated that clearing is no criterion of the completeness of digestion, and found that maximum recoveries of nitrogen were obtained 2–3 hr after clearing. His conclusions were supported by Dalrymple and King.[34] Similarly, Beet and Furzey[35] found that the use of copper sulphate as a catalyst gave results that were 2% low, unless an "afterboil" was given, and most published methods include a statement of the type "boil for 1 hr after clearing". On the other hand, Perrin[36] concluded that under the conditions used by him the conversions of nitrogen to ammonia and carbon to carbon dioxide occurred simultaneously, and no "afterboil" was needed. In general, however, it seems likely that these reactions will proceed

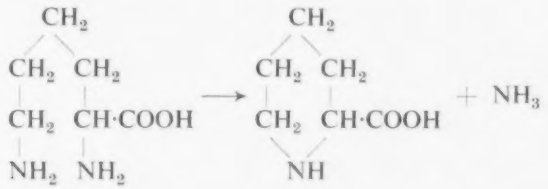
TABLE IX—EFFECT OF VARIATION IN THE AMOUNT OF MERCURY[11] OXIDE ON DIGESTION OF NICOTINIC ACID

HgO, *mg*	% N
1	8·3
5	10·75
10	11·3
20	11·3
40	11·3
100	11·2

independently, but that either or both will be influenced by the nature of the sample and the conditions of digestion. The categorical (and conflicting) statements made by different workers should therefore only be applied to the particular conditions used.

It is well-known that many pyridine derivatives (*e.g.* nicotinic acid, used in the present work) are difficult to break down under Kjeldahl conditions. Furthermore, they may not char, so that there may be no visual indication of the progress of digestion. It follows, therefore, that any compound which contains a stable heterocyclic ring, or which can give one during digestion, will not only be difficult to decompose, but may give a clear digest before conversion of nitrogen to ammonia is complete.

Sorenson and Anderson,[37] as early as 1905, realised the importance of the possibility of ring formation during digestion, but their paper appears to have been virtually overlooked by subsequent workers. They concluded that it was difficult to obtain quantitative results for lysine because it could ring-close to give a piperidine carboxylic acid. This would presumably occur through a series of reactions, the overall effect of which would be:



They demonstrated that pyridine, piperidine, and substances such as lysine and lysuric acid, which could give such a ring during digestion were difficult to decompose, whereas pyrrolidine carboxylic acid, and substances such as α-amino-δ-hydroxyvaleric acid and αδ-diamino-adipic acid, which could give a five-membered ring, were relatively easy to decompose. On the other hand, if the ring-closure could lead to a piperidone rather than a piperdine, decomposition was easy. Examples of this class were piperidone itself and substituted aminopropyl malonates.

In the light of these findings, much of the apparent contradiction and confusion in the literature becomes explicable. It is apparent that those workers who have found it necessary to use long digestion times, or who have found that a lengthy "afterboil" is necessary to ensure complete digestion, have used such mild conditions that the stable six-membered rings are only very slowly attacked. The extreme case is provided by Marzadro,[38] from whose work it appears that under very mild conditions (only 0·035 g of potassium sulphate/ml, and 30 min digestion) many pyridine rings are completely unattacked. Jonnard,[39] and Chibnall, Rees and Williams,[40] also using mild conditions, found it necessary to digest for 16 and 8 hr respectively. Jonnard, in fact, concluded that even with this lengthy digestion, it was not possible to decompose proteins completely unless a "pre-reductive" treatment was given. By his normal procedure, he obtained only 86–97% recovery from tryptophane, in agreement with Van Slyke, Hiller and Dillon,[41] who could only get about 90% recovery from tryptophane or lysine, although they tried "practically all the oxidising and catalytic agents recommended in the literature".

Dunn and Rockland[42] state, rather oddly, that "lysine may be determined quantitatively with the selenium-copper catalyst only after 50 hr digestion, whereas only 26 hr were required in the absence of selenium".

On the other hand, there are more recent workers, such as Perrin,[36] and McKenzie and Wallace,[5] who have achieved complete recovery with a much shorter digestion time (15 and 20 min respectively). They have obviously used conditions sufficiently drastic to decompose pyridine rings rapidly. Both these workers reported satisfactory results for nicotinic acid and tryptophane, and, in addition, lysine was analysed without difficulty by McKenzie and Wallace, who state that the "digestion periods used by Chibnall, Rees and Williams, and the preliminary treatment considered necessary by Jonnard, are thus an indication of failure to choose optimum conditions".

It is apparent from the above discussion that the clearing time is not a valid criterion of the rate of digestion, and observations made during the present work support this. It was, for example, observed that under some conditions complete recovery of nitrogen from benzylisothiouronium chloride could be obtained even before the mixture cleared.

As the work proceeded, it appeared that the clearing time might be dependent on the intensity of heating, as well as on the other factors studied, and an experiment was carried out to check this. Six identical mixtures were prepared, each containing 1·5 ml of sulphuric acid, 1·5 g of potassium sulphate, 40 mg of mercury^{II} oxide, and 5 mg of benzylisothiouronium chloride. These were digested as usual, and the clearing times noted.

Perrin[36] has described a "boil test" for checking the intensity of heating, and it was of interest to compare the results obtained in the above experiment with such a test. Accordingly, the time taken to boil 5 ml of water in a 30-ml Kjeldahl flask was determined for each burner. The results of both these tests are shown in Table X.

TABLE X—RESULTS OF CLEARING TIME TEST AND BOIL TEST

Burner	1	2	3	4	5	6
Clearing time, *min*	10	6·5	7	5	6·5	7·5
Boil time, *sec*	60–70	50	50–55	45–50	50	50

It is seen that the two tests show a reasonable agreement, with the exception of Burner No. 6, whose characteristics may have changed (the two tests were carried out at different times). The tests confirmed our suspicion that Burner No. 1 was less efficient than the others, and it was, for that reason, used throughout for the "blank" determination.

It is suggested that similar tests should be carried out by future authors to enable valid comparisons to be made.

When the clearing times for benzylisothiouronium chloride with varying concentrations of potassium sulphate were tabulated, it appeared that those digests containing over 2·0 g/ml were clearing more slowly than those with 1·0 g/ml. To check this unexpected finding, a series of otherwise identical mixtures (1·5 ml of sulphuric acid, 40 mg of mercury^{II} oxide, and 5 mg of benzylisothiouronium chloride) containing different amounts of potassium sulphate, were prepared and heated. The observed clearing times are shown in Table XI.

These results amply demonstrated that there was an optimum concentration of potassium sulphate for rapid clearing. Stubblefield and De Turk[24] attributed variations

TABLE XI—CLEARING TIMES WITH DIFFERENT AMOUNTS OF POTASSIUM SULPHATE

K_2SO_4, *g/ml*	0	0·5	1·0	1·5	2·0	2·5
Clearing time, *min*	16	9	5·5	9·5	11	17

in the digestion time to variations in the number of bubbles formed during boiling, and it is possible that a similar effect occurred here. Since the gas burner settings were the same for all digestions, the more concentrated solutions, having higher boiling points, boiled less vigorously than the others, and this factor may have overridden the effect of rise in boiling point. Another possible reason is that the digests containing more than 1·0 g of salt/ml frothed badly during the early stages of the digestion, and it appeared that much of the carbon was held in the relatively cool foam, almost unattacked by the boiling acid beneath.

The question then arose whether the frothing was characteristic of the sample used, or whether it was inherent at high concentrations of sulphate. Similar experiments were therefore carried out with a number of other organic compounds. In every case a minimum clearing time was observed at 1·0 — 1·5 g of potassium sulphate/ml, and in some cases the most concentrated digest tended to froth, but in no case was the frothing as severe as with benzylisothiouronium chloride.

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RECOMMENDED METHOD

(The reagents are described on p. 61)

Weigh about 5 mg of the sample into a Kjeldahl flask. Add 20 mg of mercury[II] oxide, 2·25 g of potassium sulphate, and 1·5 ml of sulphuric acid. Heat gently for 2–3 min to dissolve most of the salt, then at full heat for 20 min. The heaters should be checked with a "clearing time" test or a "boil test", as described on p. 68. The recommended times are 6 ± 1 min or 50 ± 5 sec, respectively.

Allow the flask to cool; dilute the contents with about 10 ml of water, and warm gently if necessary, to dissolve the "cake" of potassium hydrogen sulphate.

Wash the contents of the flask into a distillation apparatus, and add 10 ml of alkaline thiosulphate. Steam-distil the ammonia into 5 ml of boric acid, containing 4 drops of screened indicator. Allow distillation to proceed, at 4–5 ml/min, for 3 min with the tip of the condenser immersed in the boric acid, and a further 1 min with the tip clear of the surface. Wash down the end of the condenser, and titrate the contents of the receiver against 0·01*N* hydrochloric acid. Carry out a similar blank determination, and correct the result accordingly.

Some results obtained by this method are shown in Table XII.

CONCLUSIONS

The boiling points of solutions of up to 3·0 g of potassium sulphate in 1·5 g of sulphuric acid (2·0 g/ml) have been determined. In actual digestions, it has been found that in the absence of any catalyst, no loss of nitrogen occurs with a salt concentration of up to 2·5 g/ml (corresponding with an estimated temperature of 430°). Because of frothing and extended clearing times, however, the maximum practical concentration is 1·5 g/ml.

Mercury, used alone, is the best catalyst, under the conditions investigated. All other catalysts examined either cause a loss of nitrogen, or are inferior to mercury with regard to the rate of digestion.

Using mercury as catalyst, together with a salt concentration of 1·5 g/ml, quantitative results have been obtained on all of the compounds examined, with a digestion time of only 20 min.

TABLE XII—RESULTS OBTAINED BY THE RECOMMENDED METHOD

Compound	% Nitrogen	
	Required	Found
Nicotinamide	22·9	22·7
Histidine hydrochloride monohydrate	20·15	19·75
Lysine monohydrochloride	15·35	15·1
Tryptophane	13·7	13·6
Atropine	4·85	4·75
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine oxalate	5·35	5·4
α-Naphthoxyacetonitrile	7·65	7·7
2-Oximino-3-phenoxybutane	7·8	7·8
8-ω-Bromovaleramido-6-ethoxyquinoline	8·0	7·8
N,N-Diamyl-*N'*-phenylguanidine	15·3	15·3
1,2,3,4-Tetrahydro-β-carboline	16·25	16·0
Cyclopentylguanidine sulphate	23·85	23·8
Trimethylenethiourea	24·15	24·2

The clearing time has been shown to be of no value as a measure of the rate of digestion. The intensity of heating may significantly affect the rate of digestion, and it is suggested that future authors should carry out a "boil test", or a "clearing time" test, to enable their conditions to be duplicated by other workers.

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Zusammenfassung—Die Einwirkung des Titers der Kaliumsulfatlösung—und 21 einzelner und gemischter Katalysatoren—auf die Bestimmung des Stickstoffes mittels der Kjeldahl-Methode wurde untersucht. Quecksilber hat sich als der beste Katalysator erwiesen. Ein höherer Titer der Kaliumsulfatlösung als der sonst übliche wird empfohlen. Es werden verschiedene Faktoren besprochen, u.a. auch die "Entfarbungszeit" ("clearing time"), die sich auf die Bestimmung auswirken.

Résumé—Les effets du titre de la solution en sulfate de potasse et de 21 catalyseurs simples et mixtes sur la détermination de l'azote par la méthode de Kjeldahl, ont été étudiés. Le mercure s'est confirmé comme le meilleur catalyseur et un titre en sulfate de potasse plus élevé que le titre habituel est recommandé. La communication contient des commentaires au sujet de divers facteurs, y compris le "temps de décoloration" ("clearing time"), qui entrent en jeu dans la détermination.

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THE CO-CRYSTALLISATION OF ULTRAMICRO QUANTITIES OF MOLYBDENUM WITH α-BENZOINOXIME

DETERMINATION OF MOLYBDENUM IN SEA WATER

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Summary—The co-crystallisation of ultramicro quantities of molybdenum with α-benzoinoxime was studied and conditions were established for the quantitative recovery of this element from very dilute solution. The information derived from these experiments was applied to the isolation and determination of molybdenum in sea water. After radiometric correction for its yield, the concentration of molybdenum in sea water was determined to be 12·2 ± 0·1 μg/litre.

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INTRODUCTION

ELEMENTS are often collected and concentrated from very dilute solution by co-precipitation with an inorganic carrier. In the case of trace amounts of molybdenum, separation is generally accomplished by co-precipitation with an iron carrier. Although this procedure is effective, insoluble iron salts also efficiently scavenge many other elements; thereby the ultimate purification process may be more difficult as compared with a method which is more discriminating.

Organic reagents as a rule are more selective as carriers, and greater specificity in fact was achieved by co-precipitating molybdenum from natural waters with tannin and methyl violet.[1] Furthermore, by virtue of the ability to remove the organic reagent by simple procedures, such processes are in essence carrier-free.

As a continuation of a general study on the separation of ultramicro quantities of elements from solution by co-crystallisation with organic precipitants, the collection of trace amounts of molybdenum with α-benzoinoxime was studied. This reagent was selected because its molybdenum salt satisfies Fajans Rule.[2] The value of this rule in the choice of an organic compound was previously established.[3]

The co-crystallisation of molybdenum upon crystallisation of fractions of the carrier from solution, the influence of oxime concentration, and the effect of pH were studied. To provide for the accurate measurement of ultramicro quantities of molybdenum, a radioactive tracer was used. The information derived from these experiments was applied to the isolation and determination of the natural molybdenum content of sea water.

EXPERIMENTAL

Reagents

α-Benzoinoxime (Eastman Kodak): Purified by recrystallisation from alcohol. The purified reagent was dissolved in acetone several hr before use.

Buffer solution (pH 5·5): Prepared from analytical reagent-grade acetic acid and sodium acetate. Other chemicals used were of analytical reagent-grade.

Molybdenum-99 tracer: isolated carrier-free from a fresh uranium fission-product mixture.[4] The final solution was 0·1*N* in nitric acid and molybdenum was in the sexavalent state. Radiochemical purity was established by γ photon pulse height analysis and by decay measurements. The γ photon measurements were made in a well scintillation counter.

Spectrophotometric determination of α-benzoinoxime

To evaluate upon crystallisation the distribution of α-benzoinoxime between the liquid and solid phase, a spectrophotometric method was developed for its determination. With a Beckman spectrophotometer the maximum spectral absorption occurred at 251 mμ when α-benzoinoxime was dissolved in the buffer solution. The optical density at this wavelength of 5 to 20 μg of oxime per ml of solution when compared to a solution blank is shown in Table I. The relation between reagent concentration and optical density adhered to Beer's Law.

TABLE I.—THE OPTICAL DENSITY AT 251 mμ OF DIFFERENT CONCENTRATIONS OF α-BENZOINOXIME IN ACETATE BUFFER (pH 5·5)

α-Benzoinoxime, $\mu g/ml$	Optical density
5	0·251
10	0·495
15	0·745
20	0·985

The α-benzoinoxime distribution was determined by assay of the crystalline phase. After crystallisation, the crystals were collected on paper by filtration through a tower, then dried for several min with the aid of suction. The collected material was dissolved in absolute ethyl alcohol and diluted to a definite volume. An aliquot of this solution was diluted to the spectral working range with acetate buffer and its optical density was compared with a blank buffer solution which contained a like concentration of ethyl alcohol. The concentration of α-benzoinoxime was computed from the optical density measurement in the usual manner.

Experimental method

One ml of carrier-free molybdenum-99 with a γ photon activity of 10^4–10^5 cpm was added to 10 ml of water whose hydrogen ion concentration was previously adjusted with sulphuric acid or sodium hydroxide. Five ml of α-benzoinoxime solution were added. The resultant homogeneous solution was heated in a steam bath until part or nearly all of the acetone was evaporated. The sample was then cooled in an ice bath and the phases were separated by filtration. The molybdenum distribution was determined by γ-photon measurement of the crystal phase after solubilisation of the oxime and dilution to volume with ethyl alcohol. The measurement was made after the establishment of equilibrium between molybdenum-99 and its daughter technetium-99. This alcohol solution was analysed also for oxime.

RESULTS AND DISCUSSION

The effect of the organic reagent concentration over the range 30 to 200 mg of oxime per sample upon the co-crystallisation of molybdenum is shown in Table II. Samples were boiled until they were reduced to their original aqueous volume. At the lower reagent concentration only 15·5% of the oxime crystallised from solution and this fraction carried 25% of the molybdenum. At an oxime concentration of 120 to 200 mg per sample more than 90% of the oxime was recoverable and under these conditions molybdenum was carried quantitatively.

The effect of the hydrogen ion concentration upon the recovery of molybdenum tracer is shown in Table III. In this series the reagent concentration was 200 mg per sample. Molybdenum was quantitatively recovered over the pH range 1·8 to 5·5.

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TABLE II.—THE RECOVERY OF MOLYBDENUM AND α-BENZOINOXIME FROM SOLUTIONS WHICH CONTAIN DIFFERENT QUANTITIES OF THE ORGANIC REAGENT

α-Benzoinoxime added, *mg*	α-Benzoinoxime crystallised, %	Molybdenum-99 tracer recovered, %
30	15·5	25·0
60	68·3	85·7
120	93·3	100·0
200	91·0	100·0

TABLE III.—THE EFFECT OF pH UPON THE CO-CRYSTALLISATION OF MOLYBDENUM TRACER WITH α-BENZOINOXIME

pH		Molybdenum-99 recovered, %
(1·6*N* H_2SO_4)	0	54·6
	1·8	100·0
	3·7	99·0
	5·5	99·4
	8·0	94·6
	10·5	6·1

The recovery of molybdenum tracer was determined at pH 1·5 with 200 mg of reagent. In this series the degree of crystallisation was varied. When 58·8% of the oxime crystallised, 94·9% of the molybdenum was carried, whereas the micro component was recovered quantitatively when about 80% of the precipitant was crystallised (Table IV).

The results show that the crystalline phase was enriched with the micro component. The degree of enrichment was such that quantitative recovery of molybdenum tracer was assured when a suitable quantity of oxime was introduced into the solution.

TABLE IV.—THE RECOVERY OF MOLYBDENUM TRACER WITH DIFFERENT QUANTITIES OF CRYSTALLISED α-BENZOINOXIME

α-Benzoinoxime crystallised, %	Molybdenum-99 recovered, %
58·5	94·9
75·0	98·4
78·3	98·8
82·5	100·1
87·6	100·0
91·0	100·0
93·1	99·3
93·7	100·0

Furthermore, the optimum pH range was the same as that at which the macro precipitation reactions occur most effectively. These facts again indicate that in the co-crystallisation process the micro component combines with the organic reagent and is internally incorporated in the crystal lattice rather than surface adsorbed.[3]

Determination of the molybdenum content of sea-water

The molybdenum content of sea water has been previously reported as 0·5,[5] 3[6] and 11[7] μg/litre. The quantitative methods used were predicated upon the preliminary concentration of molybdenum from the medium by co-precipitation with an iron carrier.

The method to be described was based upon the concentration of molybdenum from sea water by co-crystallisation with α-benzoinoxime. Following this separation the oxime was eliminated by acid oxidation, molybdenum was purified by ion-exchange, and quantitatively determined colorimetrically. Radiometric correction for losses of molybdenum incurred during the analytical procedures was applied.

Separation of molybdenum from sea water

To examine the co-crystallisation of molybdenum from sea water, 1 ml of tracer was added to 10 ml of sea water previously adjusted to pH 2 with sulphuric acid. One drop of bromine was added to each of two of the four samples in the series Five ml of acetone containing 120 mg of the oxime were added, the carrier was crystallised by reducing the volume to 11 ml and the molybdenum recovery was determined. The results appear in Table V. Molybdenum was recovered quantitatively when oxidised to the sexavalent state with bromine. In the non-brominated acidified sea water samples the microcomponent was apparently partially reduced (molybdenum is sexavalent in untreated sea water[8]) and therefore incompletely recovered.

TABLE V.—CO-CRYSTALLISATION OF MOLYBDENUM IN SEA WATER WITH α-BENZOINOXIME

Sample	Molybdenum recovered, %	
	Bromine-treated	Untreated
1	99·1	
2	98·9	
3		94·3
4		93·8

Procedure

The analytical procedure was applied to surface sea water collected 40 miles due west of San Francisco. To sample aliquots of 2, 4, 6 and 8 litres was added carrier-free molybdenum tracer. The pH of the separate aliquots was adjusted to 2 with sulphuric acid. The solution was treated with bromine water (0·1 ml/litre of sample). α-Benzoinoxime was added (1·2 g in 32 ml of acetone/litre of sample). The solution was boiled until reduced to the original sea water volume. After standing at room temperature overnight, the crystals were collected on sintered-glass and dissolved therefrom with acetone. The acetone was evaporated, and the residue was wet-ashed with sulphuric acid and a 50:50 mixture of nitric acid-perchloric acid. The completely ashed and colourless solution was evaporated to near-dryness. After cooling, 15 ml of concentrated hydrochloric acid were added and

the solution was passed through a column of Dowex 2 (10 cm long, 0·6 cm diameter) previously washed with concentrated hydrochloric acid. The column was washed with 20 ml of concentrated hydrochloric acid, and molybdenum was eluted with 20 ml of 12*N* nitric acid. The eluate was evaporated to dryness, then dissolved in 1-4 ml of 8*N* hydrochloric acid. Each sample was diluted to 25 ml with distilled water and the molybdenum yield was determined radiometrically at this stage of the analysis by comparison with the molybdenum-99 control diluted to the same volume. The molybdenum content of this solution was then determined by a thiocyanate spectrophotometric procedure.[9]

RESULTS

The results of four analyses appear in Table VI. The average molybdenum content of the sea water sample analysed was 12·2 ± 0·1 μg/litre and this value is consistent with that reported by Ishibashi.[6] The main errors in the analysis are attributable to the radioactive counting statistics and the spectrophotometric measurements, and these were approximately 0·5% and 3%, respectively. Furthermore, the fact that the molybdenum content was identical for samples of different size indicates that analytical interferences were absent and that the results, therefore, are reliable.

TABLE VI.—MOLYBDENUM CONTENT OF SEA WATER

Sea water sample volume, *litres*	Molybdenum content, *μg/litre*
2	12·3
4	12·3
6	12·0
8	12·1
	Average 12·2 ± 0·1

Zusammenfassung—Die Cokristallisation von Ultramikromengen Molybdän mit Benzoinoxim wurde studiert und die Bedingungen festgestellt um dieses Element quantitativ aus sehr verdünnten Lösungen abzutrennen. Die gewonnenen Erkenntnisse wurden verwendet um Molybdän in Seewasser zu bestimmen. Nach anbringen einer radiometrischen Korrektur wurde die Konzentration von Molybdän in Seewasser zu 12,2 ± 0,1 μg/Litre gefunden.

Résumé—La cocristallisation d'ultramicro quantités de molybdène avec l'alphabenzoineoxime a été étudiée et les conditions de récupération quantitative de cet élément à partir d'une solution très diluée ont été établies. Les données déduites de ces expériences ont été appliquées à l'isolement et au dosage du molybdène dans l'eau de mer. Après une correction radiométrique pour son rendement, on a trouvé que la concentration du molybdène dans l'eau de mer était de 12,2 ± 0,1 μg/l.

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ANALYTICAL USE OF 1,3-DIMETHYL-4-IMINO-5-OXIMINO-ALLOXAN—I

DETERMINATION OF COPPER

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Summary—The use of a new organic reagent for metals, 1,3-dimethyl-4-imino-5-oximino-alloxan (DAXIM) is proposed. The acid dissociation constant of this compound has been established by potentiometric titration. The composition and the stability constant of its copper complex have been determined spectrophotometrically. An absorptiometric method has been evolved for the determination of micro amounts (1–13 μg/ml) of copper using DAXIM. The new method has proved suitable in the presence of large amounts of mercury^{II}, lead, bismuth, manganese and zinc, and of smaller amounts of iron^{III}, aluminium and certain other metals. The preparation of the reagent is described.

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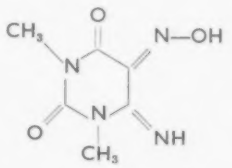
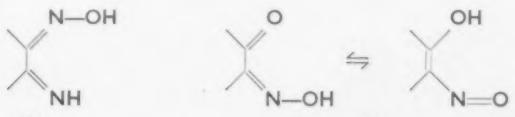
THE object of the present investigation was to find, for use as reagents for metals, organic molecules containing two or more functional groups selective for certain metals, but possessing a structure enabling them to form with a number of metals (not more than three or four) coloured, water-soluble complexes, and forming precipitates with only one or two metals. Thus it would be possible to use the same reagent, under various conditions, for the selective determination of several metals.

As a first result of the investigations, the use of 1,3-dimethyl-4-imino-5-oximino-alloxan (abbreviated as DAXIM) as an organic microanalytical reagent is suggested:



This molecule contains two characteristic functional groups: an isonitroso-imino group (1), selective for nickel and palladium^{II}, and an isonitroso-keto and nitroso-enol equilibrium (2), selective for iron^{II}, copper^{II} and cobalt^{II}:



(1) (2)

DAXIM can be prepared simply by Traube synthesis, can be purified by recrystallisation from hot water, and is an inexpensive reagent, readily available as an intermediate in the production of theophylline.

DAXIM is a crimson crystalline substance, practically insoluble in most of the conventional solvents (chloroform, alcohols, ether, dioxan, *etc.*), very poorly soluble in

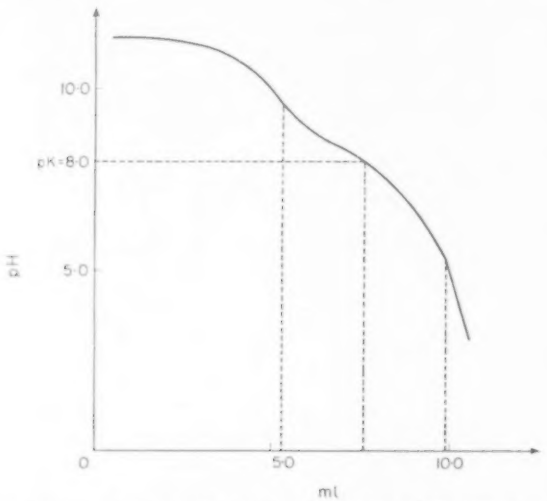


FIG. 1.—Potentiometric titration of a mixture of 0·0846 g of DAXIM and 5·00 ml of 0·2*M* sodium hydroxide with 0·1*N* hydrochloric acid using glass and saturated calomel electrodes.

acetone and in water, but readily soluble in formamide. In the present experiments, a 1–10% solution in formamide was used. DAXIM dissolves in alkalis with the formation of a brownish-red salt.

Potentiometric titration of the alkaline solution of DAXIM (Fig. 1) gave an acidic dissociation exponent, $pK = 8$.

The absorption curve (Fig. 2, curve 1) of the aqueous solution of DAXIM ($2 \cdot 10^{-2}$

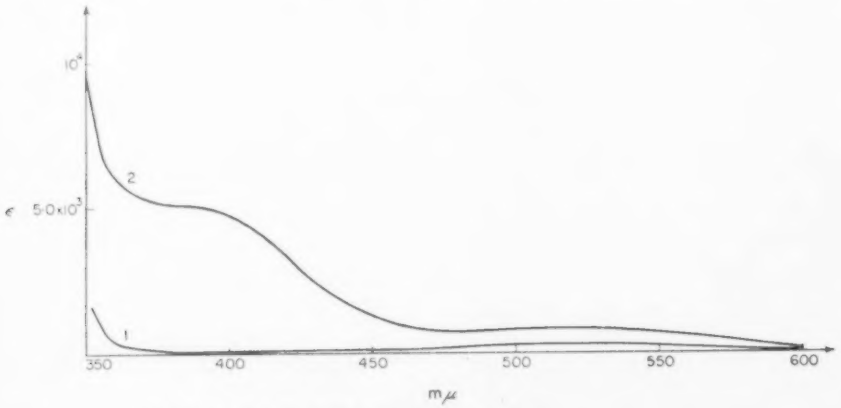


FIG. 2.—(1) Absorption spectrum of DAXIM.
(2) Absorption spectrum of the copper complex of DAXIM.

molar), containing about 4–5% of formamide, showed a maximum at 530 mμ, and no absorption was observed from 370 to 460 mμ and above 600 mμ.

As might be expected on the basis of its structure, DAXIM forms a water-soluble coloured complex with copper^{II}, iron^{II}, and cobalt^{II} ions, and a practically insoluble precipitate when boiled with palladium in a slightly acidic medium, or with nickel in ammonia.

In neutral or slightly alkaline aqueous solution, copper^{II} ions form with DAXIM a water-soluble complex, insoluble in non-polar solvents. The complex is grass-green, and shows a red tint with excess of the reagent. Its absorption curve (Fig. 2, curve 2) is

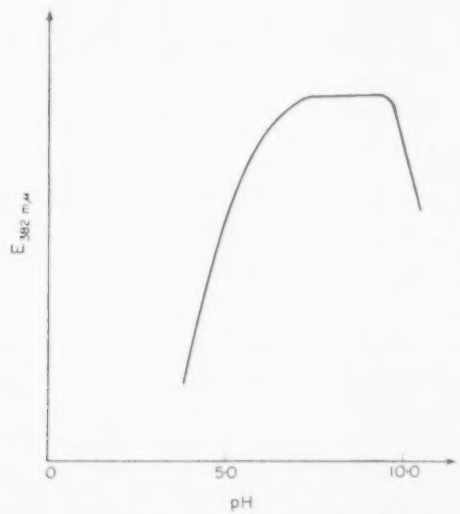
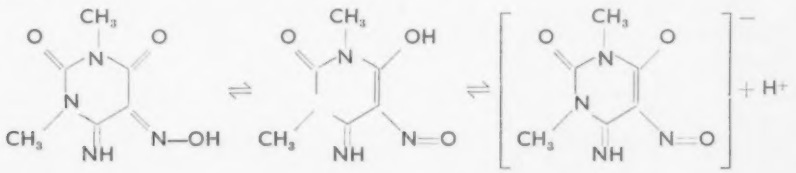


FIG. 3.—Correlation of the copper complex of DAXIM with pH values.

uniform in the range 380–390 mμ. In this region no light is absorbed by the reagent itself, and therefore in further experiments the extinction values were measured at a wavelength of 382 mμ.

The dependence of extinction values upon pH values was established at a copper^{II} concentration of $2 \cdot 10^{-4}$ moles/litre and a reagent concentration of $8 \cdot 10^{-4}$ moles/litre. As appears from Fig. 3, the maximum extinction with this concentration of the complex is between pH 7 and pH 9·5. On considering the acidic dissociation exponent of DAXIM, pK = 8, the dissociated molecules of the reagent must take place in the complex formation. Presumably a keto-enol conversion precedes the dissociation:



In order to establish the stoichiometric composition of the complex, a Job's curve[1] was plotted in a Britton-Robinson buffer of pH 8 (Fig. 4). This indicates that copper^{II}

ions form a 1 : 1 complex with DAXIM. Therefore only two of the four co-ordination points of copper may participate in the chelate formation, both residual co-ordination

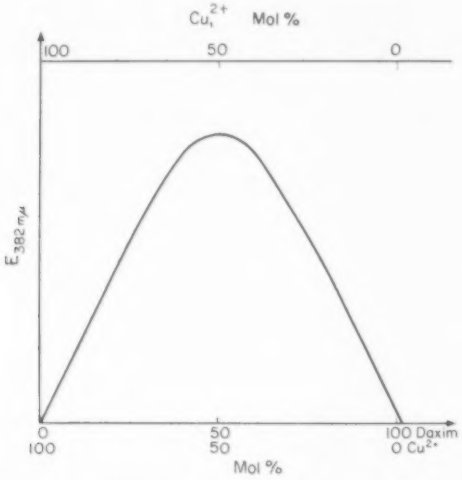
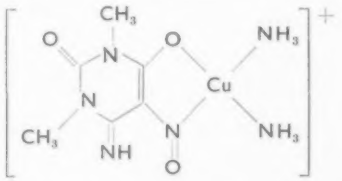


FIG. 4.—Job's curve of continuous variation. At a 1:1 ratio, the concentration of the complex was 2×10^{-4} mole/litre.

points being occupied by water molecules, or monofunctionally by DAXIM in the case of a great excess of reagent. This is why raising the excess of reagent increases the value of the extinction coefficient.

Further experiments carried out in a buffer containing ammonia suggest that in the complex formed under these conditions, two co-ordination points of copper are occupied by a DAXIM molecule and the other two by ammonia molecules:



Electrophoretic measurements also supported the above structure of the complex.

It was apparent from Job's curve, that the extinction of the complex obeys the Lambert-Beer law in the case of a large excess of reagent (over 80 mole %), and that the value of the extinction coefficient is not affected by any further increase in the excess of reagent. In further experiments the amount of reagent used was four to twenty times the theoretical value. In order to establish the molar extinction coefficient, the extinction values of various complexes prepared in copper^{II} solutions of various known concentrations (Fig. 5) were measured. It was found that in solutions containing 1–13 μg/ml of copper^{II} ions the molar extinction coefficient was

$$\varepsilon = (5{\cdot}05 \pm 0{\cdot}05) \times 10^3 \text{ (mean value of 24 measurements)}$$
at 25° and a wavelength of 382 mμ.

From the knowledge of the extinction coefficient, the stability constant of the complex was calculated using the value for the extinction measured at the maximum

of the Job's curve (*i.e.* from the extinction value of the complex of stoichiometric composition). At a given pH (pH = 8) the concentration of the ligand formed by

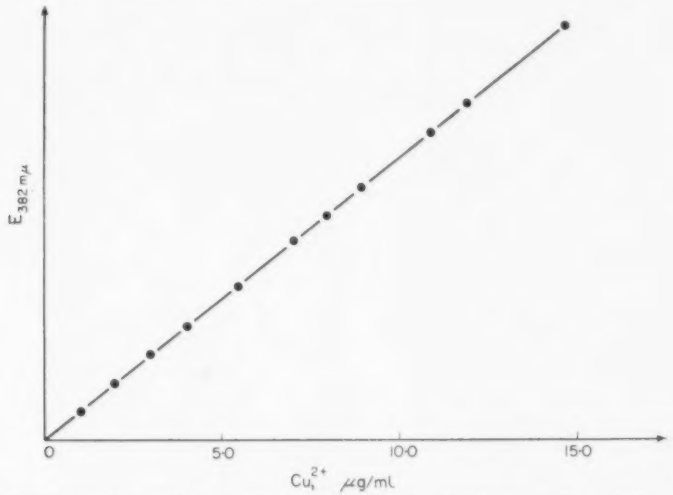


FIG. 5.—Correlation with concentration in a Britton-Robinson buffer solution of pH 8, containing 0·1% of ammonium chloride; volume, 25 ml.

dissociation of the complex was calculated from the acidic dissociation exponent of DAXIM (pK = 8) and from the dissociation exponent of ammonium hydroxide (pK = 4·74).

The stability constant of the complex is:

$$K = \frac{[Cu{\cdot}DAXIM{\cdot}(NH_3)_2{}^{+}]}{[Cu^{2+}]{\cdot}[DAXIM]{\cdot}[NH^3]^2} = \frac{1{\cdot}6 \times 10^{-4}}{1{\cdot}58 \times 10^{-24}} = 10^{20}$$

$$\therefore \quad pK = 20$$

On the basis of the molar extinction coefficients and of the calculated factor, it was possible to use DAXIM for the photometric determination of micro amounts (1–13 μg/ml) of copper[II]. Results are summarised in Table I and Fig. 5. It can be seen from Table I that the error of the method is ±2% even if the copper concentration is 1–2 μg of Cu/ml.

In order to establish how far certain metals might interfere in this determination, experiments were carried out at pH = 8 in a Britton-Robinson buffer-solution containing 0·1% of ammonium chloride and in certain cases in a buffer solution of ammonia and ammonium chloride of pH 8. The solution of unknown copper content was first treated with the reagent dissolved in formamide, and buffer solution was then added in the amount necessary to obtain a solution containing 1–13 μg of Cu/ml. In the case of metal ions which form precipitates with the buffer solution, the turbid solution was centrifuged, and the supernatant liquid was decanted (not filtered). The precipitate was stirred with a few millilitres of water and centrifuged, and the former solution was diluted with this water to known volume. Before measuring extinction values, if necessary, the solution was adjusted by further portions of buffer solution to a pH value of 7–9.

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The analytical results obtained from some experiments are presented in Table II. As can be seen, it was possible to determine about 7 μg/ml of copper with an error of

TABLE I.—DETERMINATION OF COPPER

Copper weighed, $\mu g/ml$	Extinction (382 mμ)	Copper found, $\mu g/ml$	Δ, $\mu g/ml$	Δ,%
0·96	0·076	0·958	−0·002	−0·2
	0·077	0·970	+0·01	+1·0
1·92	0·149	1·88	−0·04	−2·1
	0·151	1·90	−0·02	−1·5
3·00	0·238	3·00	0·00	0·0
	0·236	2·97	−0·03	−1·0
3·83	0·304	3·83	0·00	0·0
	0·307	3·87	+0·04	+1·0
5·00	0·397	5·00	0·00	0·0
	0·396	4·99	−0·01	−0·2
6·13	0·488	6·15	+0·02	+0·3
	0·480	6·05	−0·08	−1·3
7·66	0·608	7·66	0·00	0·0
	0·600	7·56	−0·10	−1·3
10·0	0·790	9·95	−0·05	−0·5
	0·788	9·93	−0·07	−0·7
12·04	0·953	12·00	−0·04	−0·3
	0·960	12·10	+0·06	+0·5
	1·010	12·72	−0·05	−0·4
12·77	0·995	12·54	−0·23	−1·8
	0·990	12·47	−0·30	−2·3

$\pm$2–3%, in the presence of 500 times this amount of mercury[II], of 100 times this amount of lead, and of appreciable quantities of manganese, bismuth, zinc, cadmium, iron[III] and other metals.

TABLE 2.—INTERFERENCES

Copper weighed, $\mu g/ml$	Metal ion present	Amount of metal ion present, $\mu g/ml$	Extinction (382 mμ)	Copper found, $\mu g/ml$	Δ, $\mu g/ml$	Δ,%
7·66	Hg^{2+}	4000	0·592	7·46	−0·20	−2·6
	Hg^{2+}	1600	0·596	7·51	−0·15	−2·0
	Pb^{2+}	830	0·620	7·81	+0·15	+2·0
	Bi^{3+}	250	0·610	7·69	+0·03	+0·4
	Mn^{2+}	220	0·608	7·66	0·00	0·0
	Zn^{2+}	260	0·600	7·56	−0·10	−1·3
	Cd^{2+}	440	0·589	7·42	−0·24	−3·1
	Ba^{2+}	560	0·600	7·56	−0·10	−1·3
	Fe^{3+}	68	0·620	7·81	+0·15	+2·0
	Al^{3+}	32	0·600	7·56	−0·10	−1·3
	Ca^{2+}	160	0·620	7·81	+0·15	+2·0
	Mg^{2+}	96	0·610	7·69	+0·03	+0·4
	Na^{+}	100	0·608	7·66	0·00	0·0
	Sb^{3+}	500	0·595	7·49	−0·17	−2·2

Consideration of the various methods already proposed for the determination of copper in the same concentration region shows, that of the metals listed in Table II, mercury^{II} and bismuth interfere in the dithizone method;[2] iron^{III}, bismuth and manganese in the diethyldithiocarbamate method;[3] manganese, magnesium, lead and mercury^{II} in the *m*-benzaminosemicarbazide method;[4] zinc and mercury^{II} in the urobiline method;[5] and lead and antimony in the rubeanic acid method[6].

The present investigations showed that small amounts of cobalt, palladium, nickel and iron^{II} interfere in the determination of copper by DAXIM. Thus, before using this reagent, copper must be separated from these metals and iron^{II} must be oxidised to iron^{III} with hydrogen peroxide.

Further experiments on the use of DAXIM for the selective micro-determination of other metals (palladium, iron^{II} and cobalt) are in progress.

EXPERIMENTAL

Preparation of 1,3-*dimethyl*-4-*imino*-5-*oximino-alloxan*

Reagents required

Ethanol, anhydrous.
Sodium metal.
Ethyl cyano-acetate.
Urea.
Dimethyl sulphate.
Sodium hydroxide, 40%.
Sodium nitrite.
Acetic acid, glacial.
Acetic acid, 50%.

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Preparation

Cautiously dissolve 9·6 g of small pieces of metallic sodium in 240 ml of anhydrous ethanol, then add dropwise 22·6 g of freshly distilled ethyl cyano-acetate with continuous stirring. Add 12 g of previously dried urea to the mixture, when a white precipitate which is formed will dissolve. Keep the reaction mixture boiling for 3 hr on the water bath under a reflux condenser, filter the white precipitate after cooling, dry it by suction, and dissolve it in 60–80 ml of water. Adjust the pH of this solution to 5–6 with 50% acetic acid, using universal indicator paper. Filter the precipitate of 2,6-*dioxo*-4-*imino-hexahydropyrimidine*, wash it with 2 × 10 ml of cold water and dry it at room temperature.

Treat the aqueous suspension of 12·7 g of this product dropwise under continuous stirring, with 23·8 ml of dimethyl sulphate and 25 ml of 40% sodium hydroxide. The pH of the reaction mixture must be between 8 and 9. If the liquid becomes hot, apply cooling. Stir for 2 hr, filter the precipitate of 1,3-*dimethyl*-2,6-*dioxy*-4-*imino-hexahydropyrimidine*, wash it with 3 × 20 ml of water and dry it at room temperature.

Dissolve 11·6 g of the product in 300 ml of boiling water, filter the hot solution, add 6·2 g of sodium nitrite, allow the mixture to stand for 0·5 hr, and acidify the solution with 5·6 ml of glacial acetic acid. The liquid slowly turns dark bordeaux, and 1,3-*dimethyl*-4-*imino*-5-*oximino-alloxan* (DAXIM) precipitates as crimson coloured crystals. In order to complete the crystallisation, cool the reaction mixture in melting ice, transfer the product to a filter, and dry it at 100°.

For analytical procedures the substance was repeatedly recrystallised from hot water.

Analytical method

Reagents

DAXIM in formamide: 0·05*M* (about 1%) solution.
Britton-Robinson buffer solution of pH 8, containing 0·1% of ammonium chloride.
Hydrochloric acid, 2*N*.
Sodium hydroxide, 2*N*.

Procedure:

Evaporate aliquots of the solution containing 10–130 μg of copper to 1–2 ml, neutralise approximately with 2*N* alkali or acid in the presence of universal indicator paper, and if necessary reduce again to small volume, then treat with 0·4 ml of a 1% solution of DAXIM, and with 5–6 ml of the buffer solution. If the solution contains ions forming a precipitate with the buffer solution, it is advisable to mix the reagents in a centrifuge tube, and to separate the precipitate from the supernatant liquid. On decanting the liquid, mix the precipitate with 1–2 ml of water, and again centrifuge. Measure the pH value of the combined solutions with universal indicator paper. Dilute the solution, of pH 7–9, to 10·00 ml, and measure the extinction value at 382 mμ in a 1-cm cuvette.

Multiply the extinction value by 12·6 to obtain the copper content (in micrograms) of 1 ml of solution.

In the case of higher copper concentrations, the volume of liquid can be greater (*i.e.* 25, 50 or 100 ml instead of 10 ml). Obviously, appropriately greater amounts of reagent and buffer solution should then be used.

In the present experiments, a solution prepared from exactly weighed portions of crystalline copper^{II} sulphate ($CuSO_4 \cdot 5H_2O$) of analytical grade was used, and was controlled by iodimetry and electrogravimetry.

For measuring the absorption spectra and for carrying out the photometric measurements, a Beckman DU quartz spectrophotometer and 1-cm quartz cuvettes were used, a tungsten filament serving as light source.

Acknowledgement—Thanks are due to Mr. L. Ladányi for carrying out the organic preparative procedures.

Zusammenfassung—1,3-Dimethylalloxan-4-imid-5-oxim (DAXIM) wird als neues Reagens für Metallionen vorgeschlagen. Die saure Dissoziations-konstante der Substanz wurde durch potentiometrische Titration ermittelt. Die Zusammensetzung des Kupferkomplexes der Substanz wurde photometrische bestimmt und die Stabilitätskonstante berechnet. Eine photometrische Mikromethode (1–13 μg per ml) zur Bestimmung von Kupfer wurde entwickelt. Die Methode arbeitet korrekt in Gegenwart grosser Mengen von Quecksilber (II), Wismuth, Blei, Mangan und Zink sowie kleineren Mengen von Eisen (III), Aluminium und einer Anzahl anderer Metalle. Die Synthese des Reagenzes ist beschrieben.

Résumé—L'auteur propose l'utilisation d'un nouveau réactif organique pour les métaux, la 1,3-diméthylalloxane-4-imide-5-oxime (DAXIM). La constante d'acidité de ce composé a été établie par titrage potentiométrique. La composition de son complexe avec le cuivre a été déterminée par photométrie et sa stabilité a été mesurée. L'auteur quantités (1–13 μg par ml) de cuivre, utilisant la DAXIM. La méthode convient en présence de grandes quantités de mercure (II), plomb, bismuth, manganese et zinc et de plus faibles quantités de fer (III), aluminium et d'un certain nombre d'autres métaux. La préparation du réactif est décrite.

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A CRITICAL EXAMINATION OF THE GRAVIMETRIC AND TITRIMETRIC METHODS FOR THE DETERMINATION OF GOLD

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Summary—This survey covers pertinent literature published before July 1960. An attempt has been made to identify the most generally applicable titrimetric and gravimetric methods for determining gold. While certain methods have been rejected from this point of view, it is admitted that, where many determinations are involved and the qualitative compositions are approximately constant, some of these methods may be particularly effective. Because of its wide application, the precipitation of gold from cyanide solutions is treated separately. The controversial character of the iodometric method for gold has been emphasised.

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THE origins of methods for extracting gold from natural sources reach far into antiquity. From the very advent of scientific literature extractive procedures have been recorded, until at the present time the separation and determination of gold is a subject of discussion in practically all issues of chemical abstracts. Because of the wide applications of this metal, extending as they do into the fields of medicine, decorative alloys, monetary systems *etc.*, extractive methods are of many types, among which solvent extraction processes predominate. A rather wide choice of these is available and they include treatment of both fused and aqueous systems.

Initially it was hoped to discuss in a single review the recorded methods of isolation and determination but the large accumulation of pertinent literature made this inadvisable. The present review will be confined to the classical methods of determination; and subsequent discussions will deal with the "instrumental methods" and the procedures for isolating gold from both solid and liquid systems. More than one hundred published procedures deal specifically with the gravimetric determination of gold, and at least as many more are concerned with this determination as an integral part of a more general analytical scheme. This situation is not surprising, since a large number of available methods for a metal constituent is practically always associated with the ease of discovery of new reagents for that constituent: and few metals respond to a greater variety of precipitants. Generally this characteristic is found with predominately bivalent or quadrivalent metals; but in the case of gold, with a reduction potential of $-1{\cdot}4$ V, the quantitative precipitation of the metal is accomplished with ease.

GRAVIMETRIC METHODS

Quantitative reduction to metal

In general, the quantitative recovery of metallic gold requires exacting techniques. To avoid loss of the fine but heavy particles of gold, one must recognise the effects of acidity, rate of addition of precipitant, period of digestion and particularly the

tendency for these particles to adhere tenaciously to beaker walls. The techniques used by the present author include the initial addition of the precipitant by means of a fine capillary and the final transference of gold in the light of a flashlight placed upright beneath the beaker, assisted further by a small piece of ashless paper moved about by a stirring rod drawn to a fine stem which terminates in a small glass globule. Alternatively one may use a filtering feather sealed directly into a glass rod. As one would expect from the pertinent reduction potentials, the tendency toward the formation of fine particles will vary with the reagents used.

The optimum heating range for precipitated gold has been the subject of various investigations. Ishii[1] recommended temperatures above 230°. Kiba and Ikeda[2] used 700°. Champ, Fauconnier and Duval[3] recorded useful data which provide some explanation for the variety of optimum ignition temperatures. As one would expect, occluded organic reductant will have some influence, but a hitherto unknown phenomenon was observed in that "gold retains an amount of oxygen by adsorption, which varies according to the degree of subdivision, the nature of the precipitating reagent, and the environmental atmosphere during heating. When this phenomenon takes place the gain in weight is about 1%. It is reversible, and if the cooling curve is identical with the heating curve, exactly the same amount of oxygen is released as was taken up on heating". This characteristic is made clearly evident by heating gold precipitated by pyrogallol.

Among the many available reductants the following are more generally used: oxalic acid, sulphur dioxide, ferrous sulphate, nitrous acid, hydroquinone, dimethylglyoxime, stannous chloride, hydrogen peroxide and formic acid. Of these the first three have been most frequently applied.

In 1841 Kemp[4] used oxalic acid to separate gold from platinum, and over a century later Magdalena[5] recorded detailed directions for this precipitation. Malowan[6] recommended the addition of morpholine oxalate to the oxalic acid solution to produce an easily handled precipitate. With oxalic acid there is the advantage that excess reagent presents no problem, and the reagent is stable and readily obtained in a pure state. On the other hand a successful precipitation is peculiarly dependent upon the prior history of the gold solution. Samples which have been treated with *aqua regia*, and subsequently with hydrochloric acid, yield exceedingly fine precipitates, sometimes with a marked tendency to adhere tenaciously to the beaker walls; and not infrequently the precipitation is incomplete. These difficulties become much less evident when oxalic acid is used to precipitate gold from solutions of its pure salts. The exact cause of this difference in behaviour is not clear. In any case this method usually requires extended digestion, and other reductants are much more suitable for general work.

Ferrous sulphate and sulphur dioxide have been widely used. The former may be objectionable when a separation from other noble metals is to be achieved, since iron may interfere in subsequent precipitations. Sulphur dioxide may also interfere with subsequent determinations, *e.g.* platinum metals, and it is usually removed from the filtrate by evaporation with hydrochloric acid.

Oxalic acid, ferrous ion and sulphur dioxide are particularly sensitive to the presence of nitric acid, which must be removed before precipitation. Unless care is exercised, the required evaporation with hydrochloric acid may result in the reduction of gold. This may be avoided by the addition of sodium chloride. When the presence

of salt is to be avoided, one can accomplish a satisfactory evaporation with acid alone, by watchful care and the use of small volumes of acid. The intermittent addition of large volumes of hydrochloric is always inexcusable. The use of a few ml total of acid permits the removal of nitric oxides within a few minutes. Both ferrous ion and sulphur dioxide are used in acid media, and the resulting gold is usually free from large proportions of impurities.

In 1887 Bettel[7] and Kruss and Hoffman[8] reviewed the relative efficiency of ferrous sulphate, oxalic acid and sulphur dioxide as reductants for gold. It was concluded[8] that gold was selectively reduced by the three reagents in the presence of ruthenium, rhodium and iridium, but in the presence of platinum, oxalic acid was the preferred reagent, and in the presence of palladium, sulphur dioxide was recommended. In 1937 Beamish, Russell and Seath[9] rejected both oxalic acid and sulphur dioxide as specific reductants, the former partly because of a persistent tendency to carry palladium, and the latter because of significant adsorption of platinum. Because of the tendency for the sulphur dioxide precipitate to adsorb platinum and palladium, Swanger[10] recommended re-precipitation by oxalic acid or nitrite. Lenher *et. al.*[11] preferred ferrous sulphate and nitrous acid to sulphur dioxide for the separation of gold from tellurium. With the former reagent a 1–2% hydrochloric acid solution and a digestion period of 24 hours were recommended. To precipitate one part of gold from one thousand million parts of solution, Pollard[12] co-precipitated gold with tellurium by sulphur dioxide from 1·2*N* hydrochloric acid. Hecht and Lamac-Brunner[13] recorded procedures for the microgravimetric determination of gold by sulphur dioxide, ferrous sulphate, hydrogen peroxide, sodium dihydrogen phosphate, 8-quinolinol and hydrogen sulphide. While little new information was provided, the publication includes an acceptable list of procedures.

Precipitation by hydrogen peroxide is one of the least acceptable methods for the reduction to gold, since the basic medium required almost eliminates any separational value and encourages the formation of a fine precipitate. Vanino and Seemann[14] partially avoided these difficulties by digesting the basic mixture to destroy hydrogen peroxide and subsequently acidifying with hydrochloric acid. Ivkovich and Shaula[15] applied a similar procedure for the precipitation of gold by superoxide from solutions containing copper and cadmium. Rossler[16] considered the peroxide reduction in acid solution as too slow to be of practical value, and recommended the addition of lithium or potassium carbonate.

Formaldehyde was used by Vanino[17] in an alkaline medium and by Awerkieff[18] in an acid medium. Neither is recommended as reasonably selective. A similar objection applies to reduction by hydrazine salts. Christensen[19,20] and Plaksin and Koyukhova[21] thus reduced gold salts in acid solution and Stammreich[22] used an ammoniacal medium.

An interesting method of determining very small amounts of gold was described by Donau.[23] The minute amounts of gold were deposited from the boiling acid solution upon small pieces of Japanese silk, which was subsequently burned on platinum foil to form an alloy which could be weighed. Associated base metals did not interfere.

Sodium chlorite[24] and hypophosphorous acid[25] have been used as reductants for gold. The former allows separation from the platinum group, while the latter will separate gold from platinum only in the absence of palladium. For general purposes neither method is recommended.

Sodium nitrite is one of the oldest and most generally used precipitants for metallic gold. An interesting application was described by Jameson,[26] who added sticks of potassium nitrite to an aqueous solution of gold, followed by concentrated sulphuric acid. The gold precipitated within a few minutes as large nodules which could be separated by decantation. Holzer and Zaussinger[27] used sodium nitrite to precipitate gold from very dilute hydrochloric acid solutions of decorative platinum alloys. Subsequently the solution was neutralised to a phenolphthalein end-point, and the filtered gold was purified by treatment with nitric acid solution. Gilchrist[28] used sodium nitrite to precipitate gold at a pH of about 1·5 (red-orange of thymol blue). The procedure contains directions for the simultaneous precipitation of indium, copper, zinc and nickel, and the subsequent selective acid extraction of the base metals. This author emphasised the precaution of washing out the nitrite before acidification of the hydroxide precipitate, to avoid dissolution of gold. Later, Gilchrist[29] stated that the reduction of gold by sodium nitrite is complete at the end-point of chlorophenol red (pH 4·8–6·4).

Hydroquinone has proved to be an effective reductant of gold in fire assay beads.[9] As compared with the older reducing reagents, there is less interference from platinum and palladium; the latter metal may be removed directly from the filtrate, but for the subsequent determination of platinum the organic matter should be destroyed. Some eight related organic reductants proved to be suitable quantitative precipitants. Procedures have been recorded for the application of hydroquinone to the analysis of alloys of copper, nickel, zinc and gold,[9] for the separation of gold from tellurium and selenium[30] and for the analysis of mill cyanide solutions.[30]

Organic precipitants

A considerable number of organic reagents have been used for the determination of gold, some of which produced either mixed precipitates or precipitates not easily freed of excess precipitant. In these instances ignition to gold is required. Relatively few organic precipitants produce easily prepared pure substances.

Citarin,[31] urotropine,[32] 8-quinolinol, tetra-ethylammonium chloride,[33] mercaptobenzothiazole[34] and dimethylglyoxime[35,36] have been used successfully. Citarin and urotropine are used in basic media and produce metallic gold. 8-Quinolinol[37] is used in ammonium acetate medium producing a mixed precipitate requiring ignition to metal. This method is not recommended. Tetra-ethylammonium chloride was used by Maynard[33] to avoid the contamination of gold by platinum and palladium associated with sulphur dioxide precipitations. The procedure involved prior precipitation by sulphur dioxide, then re-precipitation by the tetraethylammonium chloride to produce a yellow precipitate of variable composition which required reduction by sucrose before heating. The method has little or nothing to recommend it. Kuras and co-workers[34,38] used mercaptobenzothiazole in alcohol which, subsequent to the evaporation of the alcohol, precipitated a complex which was then ignited to gold. Duval[3] found that the complex was unstable and impure. For general quantitative work the method has little to recommend it. Dimethylglyoxime was first used by Wunder and Thuringer[35] as a precipitant for palladium. These authors stated that in hot hydrochloric acid metallic gold was precipitated, but no quantitative results were provided. Under similar conditions the present author[39] has isolated an organic complex which rapidly decomposed on exposure to air producing metallic gold. The

composition of the yellowish plates proved to be variable, which state of affairs could be the result of rapid decomposition or of the formation of mixed crystals. In any case continued heating of the precipitating medium produced gold quantitatively.[36]

A few reagents produce organic weighing forms with the great advantages of easy transference and purification and also of providing very favourable weight factors. The thionalide of gold was suggested as a direct weighing form by Berg and Roebling,[40] but the present author has been unable to find a recorded procedure. Unemura[41] recorded the proper heating temperature as 230°. From the general failure of this reagent to provide weighing forms in its wide applications as a precipitant for other metals, one is not encouraged to expect an easily obtained pure substance with gold, nor any useful degree of specificity.

The first organic-gold weighing form was recorded in 1946.[42,3] Thiophenol in acid solution precipitated a white compound which upon ignition yielded slightly high results.[42] Duval[3] found that "the white deposit turns yellow on prolonged exposure to light, dries immediately, and has a constant weight up to 157° which satisfies the formula C_6H_5SAu to within 0·5%". The two levels of the pyrolysis curve could be used for automatic determinations since the ignited gold gave no evidence of adsorption of oxygen. Deterrents in the use of the method are the instability and disagreeable odour of the precipitant and the objectionable odour of the ignited products. Furthermore, the method is far from specific with respect to interference from platinum metals. Both platinum and palladium are quantitatively precipitated, although the associated base metals, copper, nickel and iron do not interfere.

A promising gravimetric method for gold was proposed by Harvey and Yoe.[43] The sodium salt of *N*-(*N*-bromo-*C*-tetradecylbetainyl)-*C*-tetradecylbetaine produced two complexes; one in hydrochloric acid solution containing 22·14% gold, and a second in hydrobromic acid solution containing 18·01% gold. Both could be dried to constant weight at 85°. Precipitation from hydrochloric acid resulted in coarse flocculent particles which decreased in size as the reagent was added to such a degree that filtration and washing were objectionably difficult. With 1–3*N* hydrobromic acid these processes were not adversely affected. The precipitate of unknown constitution could be weighed directly or ignited to gold, and the recorded results indicated excellent recovery over the range of about 5–10 milligrams of gold. However, precipitations at 30° or higher were incomplete, and large excesses of reagent reduced the particle size, with excesses beyond 25% increasing the solubility of the precipitate. The reagent is far from specific, with interferences from most of the platinum metals and a variety of base metals. Unfortunately the effects of iron, copper and nickel were not discussed, although a procedure was applied satisfactorily to gold ores which involved a solvent extraction in the presence of platinum metals, and in general a co-precipitation with tellurium by tin^{II} chloride. The method will have excellent application for standardisation and similar purposes, but in spite of the favourable weight factor, the relative value of the method for complex materials is quite limited.

Mahr and Denck[44] precipitated $AuCr(NH_3)_2(SCN)_4$ from a nitric acid solution containing sodium dihydrogen arsenite and Reinecke's salt. After a short digestion period, the precipitate was washed with dilute hydrochloric acid, dried and weighed. Bagbanly[45] also used Reinecke's salt in a hydrochloric acid medium and dried at 110°. This reaction is not particularly sensitive, and although it is stated

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that silver, mercury and thallium interfere, there is no reference to the effect of other noble metals; furthermore, no recovery values are recorded. In the present author's opinion better methods are available.

Metal reductants and other methods

Except as applied to cyanide solutions of gold, metal reductants offer few if any advantages. In some instances, for no apparent adequate reason, the precipitated gold was amalgamated with mercury which was then selectively removed. Thus Kalishev and Serebrennikov[46] used zinc and then mercury, with the claim that gold formed a compact, easily weighed residue. Tananaev and Davitashvili[47] used a tin amalgam in sulphuric or hydrochloric acid to complete a precipitation of gold and platinum in 5–10 minutes. Austin[48] used mercury to precipitate and collect gold from a solution of ore, and selectively removed mercury by nitric acid. This wet assay of ores and that of Harvey and Yoe[43] are worthy of further examination.

To a very limited degree, fuming with high-boiling acids may be applied to precipitate gold from aqueous media. Platinum may thus be co-precipitated, although with relatively less efficiency. Protopopescue[49] dissolved a gold alloy, removed silver chloride, and fused with potassium hydrogen sulphate to precipitate gold. Caul and Schoonover[50] adapted the sulphuric acid fuming procedure to the analysis of gold in dental amalgams. The insoluble material from a nitric acid solution was fumed with sulphuric acid to isolate gold selectively. Silverman[51] used fuming with perchloric acid to separate gold from aluminium-copper alloys after dissolution in nitric-hydrochloric acids; the isolation of gold was completed by treating the perchloric solution with formic acid to separate the traces remaining in solution. One cannot recommend this method, and in general these acid extractions will have few advantages over the more formal approaches.

A rather unusual method for the determination of gold was used by Caley[52] for alloys of high gold content. Its special value for the determination of gold in valuable objects is evident. The method involves the determination of the density of the object and the application of the tea-mixing rule, and depends upon the high density and content of gold, the assumption that the gold is mechanically mixed, a reasonably accurate knowledge of the qualitative composition of the object and other data. In favourable cases the accuracy of the determination can be quite high. The method will have an excellent application in naturally occurring quartz containing gold nuggets.

METHODS FOR CYANIDE-GOLD SOLUTIONS

Because of the extensive industrial applications of cyanide solutions for the extraction of gold from ores the analytical methods applied to these solutions will be discussed collectively. Although the number of pertinent publications during the past four decades is large, few outstanding innovations have been introduced into the older methods. One of the most widely used of the older procedures was developed by Chiddy,[53] and according to Bugbee[54] "is used almost exclusively in this country for the assay of cyanide solutions. It works equally well on strong or weak, foul or pure solutions, and almost any quantity may be taken". The method involves addition to the cyanide solution of lead acetate-acetic acid solution and fine zinc shavings or zinc emulsion. Finally hydrochloric acid is added to the hot solution to

remove excess zinc. The supernatant liquid is decanted, and the sponge is pressed into a compact mass and cupelled.

Wogrinz[55] rejected the Chiddy method when the cyanide solutions contained ferrocyanide, but this, however could be destroyed by evaporation to a residue, and then fuming with sulphuric acid. After treatment with *aqua regia*, hydrochloric acid, lead acetate and zinc powder, the gold was collected, washed, ignited and weighed. Roodhouse[56] modified the Chiddy method slightly by adding acetic acid to the reduced mixture, followed by boiling, decantation and addition of hydrochloric acid. Bugbee[54] stated that "the Chiddy method with its numerous modifications is reported to be unpopular on the Rand on account of the care required if satisfactory results are to be obtained and because it requires the application of heat". The alternative procedures, used in the absence of thiocyanates, involve the addition of copper^{I} chloride in hydrochloric acid or the production of copper^{I} ion *in situ* by adding consecutively a saturated solution of sodium cyanide, copper sulphate, sodium sulphite and sulphuric acid. Potassium ferrocyanide is added in small amounts to provide a carrier and to aid in filtering. With the last two methods the gold is first precipitated as $CuAuCn_2$, and the excess cyanide removed as copper^{I} cyanide. The precipitation is accomplished in the cold. The use of potassium ferrocyanide as a coagulant was rejected by Creed and Cayton-Boxall[57–59] as unnecessary and leading to losses when excess is present. King and Wolfe[60] provided an improved copper^{I} chloride procedure which required the use of the ferrocyanide as a coagulant, and the authors cautioned against the presence of an excess. The precipitate and filter were subsequently fire-assayed.

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To avoid the necessity of destroying cyanide before determining gold, Bettel[61] used a zinc-copper couple obtained by adding to a strong cyanide solution copper^{I} cyanide and zinc fume. For approximate work colorimetric methods were used, but for accurate analysis the precipitated gold was freed from zinc and organic matter. In a later publication Bettel[62] followed the copper^{I} chloride precipitation by a treatment of the fitrate with zinc and lead acetate in excess hydrochloric acid. In 1934, Ageenkov *et al.*[63] stated that the recorded methods for sampling and analysing cyanide solutions yielded very inaccurate results.

A wide variety of reducing reagents have been proposed for the reduction of gold salts in cyanide solutions. Bayula[64] used carbon, and subsequently fire assayed the precipitate. For the determination of gold in cyanide plating solutions, Kushner[65] rejected the classical reduction methods for routine purposes because of the excessive time and the tedious techniques required, and the sulphuric acid evaporation method because of a tendency toward the formation of colloidal gold and of the poisonous fumes evolved during the heat treatment.[66,67] The method proposed by him included the removal of free cyanide by the addition of silver nitrate and subsequent fuming with sulphuric acid. Methods such as these are far from specific. The noble metals and associated base metals interfere, although slight modifications could be applied to ensure satisfactory recoveries.

Nitric acid was used by Marenkov[68] to isolate gold in cyanide slimes, subsequently dissolving it in *aqua regia* and re-precipitating by hydrazine hydrochloride. Seath and Beamish[30] used zinc in mill-cyanide solution to precipitate gold, tellurium and silver collectively; the mixture was then dissolved and treated with hydroquinone to remove gold selectively. Shah[69] also used zinc, the excess being removed in a sulphuric

acid solution. The gold was purified by nitric acid before weighing. Rochat[70] used aluminium foil to isolate gold, which was then purified by nitric acid within an error of 0·5%. Aluminium sheet has been used in a modification of the Chiddy method.* After the removal of lime by sodium hydroxide and filtration, the sheet is completely immersed. The resulting sponge is coherent and relatively free from impurities. Presumably the method requires the presence of silver. The chemical explanation of the procedure presents an interesting problem.

The simultaneous precipitation of gold and mercury has been used as an analytical method. Thus Caldwell and McLeod[71] treated a "simulated cyanide solution" with a large excess of ferrous sulphate to convert the cyanide to ferrocyanide, then mercuric chloride solution and magnesium powder and concentrated hydrochloric acid. After standing overnight the mercuric-gold mixture was decanted and filtered, lead was added, and the gold was isolated by cupellation. It is surprising that the author offers no comment concerning the possibility of gold losses in the presence of potassium ferrocyanide, since such a loss has been emphasised by assayers,[60,72] who recommended only very small amounts of ferrocyanide to provide a carrier in the copper^{I} chloride method. While the results provided by Caldwell and McLeod, by Smith[72] and particularly by Wogrinz[55] (who stated that the method of Chiddy[53] was inapplicable in the presence of ferrocyanide) indicate low recoveries, the values are quite comparable to those recorded for the older-established procedures. Obviously there is here a problem of some practical significance. The mercury-gold collection was also used by Lundquist[73] who treated the cyanide solution with zinc dust, and then with mercuric chloride. After warming of the solution, hydroxylamine hydrochloride and ammonium hydroxide were added and the excess zinc was dissolved by hydrochloric acid. The gold amalgam was treated with nitric acid to remove all traces of mercury, and the zinc was then annealed and weighed. Wilson[74] provided elementary details for the determination of gold in cyanide solutions by ferrous sulphate and oxalic acid, after elimination of hydrogen cyanide by hydrochloric acid. Precipitation by zinc was discussed, and a method was proposed which involved evaporation of the cyanide solution to a syrup, addition of litharge, evaporation to dryness, and heating the residue to form a button. The lead was selectively parted by nitric acid. Cadmium sulphide powder has been used to precipitate gold sulphide from an acidified solution of cyanide electrolyte.[75] The precipitate was then ignited, treated with nitric acid and finally converted to gold at 800–900°.

TITRIMETRIC DETERMINATIONS

Most of the titrimetric procedures for gold require a precipitation of the metal or of the aurous salt. In all but the iodometric gold methods, the end-points are determined through potentiometric techniques or by back-titrations against excess of reductant. As would be expected from the reduction potentials of gold salts, there is available a wide variety of reducing agents. Among the most suitable are hydroquinone, iron^{II}, arsenite ion and ascorbic acid. Others of use for specific purposes, but not recommended for general use, are titanium^{III}, tin^{II}, chromium^{II}, copper^{I}, hydrazine salts, sulphur dioxide, *etc.*

Potassium iodide is a notable exception to the general type of reductant involved

* Private communication from S. E. Wolfe.

in gold titrations. One of the earliest reagents, it was used in 1899 by Peterson,[76] who suggested that the reaction resulted in the stoichiometric formation of univalent gold iodide and free iodine, the former reacting with sodium thiosulphate to produce $NaAuS_2O_3$. Thus Peterson believed that the quantitative relationship was one atomic weight of gold to three formula weights of sodium thiosulphate. Whether or not the above gold complex is formed, there can be little doubt that the proposed equation is unacceptable. In any case, Gooch and Moreley[77] indicated that the relationship of gold to iodine is 1:2, and found "no evidence whatever" for the reaction to form $NaAuS_2O_3$. These authors used amounts of gold of the order of 1 mg or less, and recorded that the reaction was influenced by the "volume of the solution, the mass of iodine present, and the time of action". To avoid the presence of foreign oxidising substances during the dissolution of gold by chlorine water or *aqua regia*, the solution was twice treated with ammonia in excess, boiled, and acidified with hydrochloric acid. The titration procedure involved the addition of excess potassium iodide just sufficient to dissolve the gold-iodide. The liberated iodine was titrated with standard sodium thiosulphate to a clear solution in the presence of starch and then standard iodine was added to the rose-coloured end-point. Excellent results were obtained with 0·01*N* or 0·001*N* solutions of the titrant, and in general the work of these authors reaches a high standard. Scott[78] records the above method for small amounts of gold, but, without explanation, recommended the determination of an experimental gold factor for the standard thiosulphate solution.

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For larger amounts of gold the Gooch and Morley method has been found inapplicable. Rupp[79] ascribed the difficulty to the instability of gold^{I} iodide, which slowly dissociated into gold and iodine. Herschlag[80] rejected the suggestion that the instability of gold^{I} iodide was a main cause of error, and without sufficient experimental evidence he claimed that the error was caused "by a side reaction involving the aurous iodide complex and thiosulphate". This statement was made as a result of Lenher's[81] ability to obtain accurate results on samples of gold ranging from 0·0395 to 0·7301 g by a titration of released iodine with a standard sulphurous acid solution, in which the back-titration with iodine used by Gooch and Morley was not required. Vanning and Hartwagner[82] rejected Peterson's method because the calculations based on the assumption of one formula weight of gold to three of sodium thiosulphate produced high experimental results; and they rejected Gooch and Morley's method because of inaccuracy which became more evident when larger amounts of gold were used. The proposed method depended upon the oxidation of excess potassium iodide by $6AuCl_3 \cdot HCl$ to produce 12I and 6HCl, the latter producing 6I in a solution containing potassium iodide and iodate, a final relationship of 18I to 18 formula weights of sodium thiosulphate. The results obtained in pure $HAuCl_4$ solution were an improvement on those from older methods, but the method will have a very limited application since acids other than the combined hydrogen chloride are inadmissible. Unfortunately these authors' report[82] included no reference to the preparation of gold solutions by dissolution of the metal.

Herschlag[80] recorded one of the most acceptable iodide procedures. Here the interference from the nitric-hydrochloric acid dissolution of the gold was removed by treating with sodium hypochlorite or by potassium chlorate, diluting and boiling out the excess chlorine. The solution was then neutralised with sodium carbonate, slightly acidified and made basic to litmus with sodium hydrogen carbonate. Unlike

in the earlier treatment with ammonia, no precipitate appeared during this neutralising process. Excess potassium iodide was added rapidly to avoid the oxidation of iodine by gold^{III} chloride, and the liberated iodine was titrated with standard 0·01*N* sodium arsenite. The latter was standardised by iodine, and the gold content was calculated stoichiometrically. The method was applied to pure gold solutions, gold in cyanide solutions and gold solutions containing copper, iron, silver and nickel. Interference occurred when the coloured precipitates in the basic medium interfered with the starch end-point. The colour of platinum and palladium iodide complexes also caused some interference. The recoveries on samples of 20–400 mg of gold were exceptionally accurate. The above procedure has been recommended by Young[83] who reviewed various titrimetric methods for gold.

With the exception of Peterson's explanation[76] for the gold iodide reaction there has been general agreement that the ratio of reactants is one atomic weight of gold to two atomic weights of iodine. In all cases excess of potassium iodide has been used in both acid and basic solutions of gold^{III} chloride. However, Brull and Griffi[84,85] have applied successfully a procedure based on the reaction:

$$2AuCl_3 + 6KI = 6KCl + Au(AuI_4) + I_2 \qquad (1)$$

rather than the generally accepted reaction:

$$AuCl_3 + 3KI = 3KCl + AuI + I_2. \qquad (2)$$

Inexplicably, the experimental results which have been recorded for both relationships have been quite acceptable. Brull and Griffi recommend their method for quantities of gold of the order of 1 to 2 mg. With about 10 mg there was some indication that the reaction (2) became effective. Variation in the proportion of potassium iodide appeared to be without effect. Attempts to isolate the complex $Au(AuI_4)$ failed. The authors found that copper did not interfere[85] provided that the excess of potassium iodide was not too great. It is unfortunate that the publications dealing with this important iodometric method contain insufficiently complete information concerning the influence of acidity, iodide concentration, optimum amounts of gold, *etc.* The provision of the information which is lacking would be a useful contribution.

Parker[86] used a method somewhat similar to Herschlag's to determine gold in plating solutions containing nickel and copper. However, cyanide was eliminated by treatment with nitric and hydrochloric acids and nitrite with sodium hypochlorite. There was no interference from iron^{II}, iron^{III}, zinc, stannate^{II}, nickel, silver, copper^{I} or copper^{II}. Sudilovskaya[87] rejected the mixed acid method for the elimination of cyanide interference, and recommended treatment by repeated evaporations, fusion with metallic sodium and treatment with concentrated sulphuric acid.

An unusual back-titration was proposed by Lespagnol and Merville,[88] who precipitated gold by formaldehyde and treated the precipitate in a hydrochloric acid medium with standard 0·1*N* iodine and a solution of potassium iodide. The excess iodine, residual from the dissolution of gold^{I} iodide, was titrated with 0·1*N* sodium thiosulphate. The method was applicable to medicinals, *etc.*

A unique iodometric method, and one worthy of further attention, was recently described by Riolu and Garrini[89]. These authors treated solutions of 1–7 mg of gold^{III} salt with an excess of 0·01*M* sodium chlorite. The stoichiometrically formed chlorine dioxide was swept from the mixture by carbon dioxide over a period of 1 hour or more

and collected in a solution containing sodium iodide and hydrochloric acid. The liberated iodine was titrated with sodium thiosulphate. There was no interference from silver, copper, zinc, nickel, iron, platinum and cadmium. The error was less than 1%. Someya[90] used potassium iodide to titrate gold^{III} chloride in slightly acid solution potentiometrically. The first discontinuity was the result of reduction of the chlorine used to oxidise the gold to the tervalent state; this was followed by the discontinuity due to gold^{I} iodide. Copper did not interfere. The author discussed the potentiometric methods for selenium, tellurium and gold.

An interesting application of the gold iodometric determination was described by Murray and Krige[91]. In an attempt to find a wet method for the gold assay of ores these authors digested the sample with bromine water or *aqua regia*. The filtered solution was finally titrated potentiometrically with 0·01*M* potassium iodide using saturated calomel and platinum wire electrodes with a potassium chloride-agar bridge. The end-point was accepted as the maximum value of the ratio of voltage to volume of titrant. For various reasons only very small concentrations of hydrochloric and nitric acids were admissible. This method may find useful application to a restricted type of ore, but because it is time-consuming and subject to a variety of interferences it is not recommended for application to gold ores in general. While the results agreed fairly well with the classical assay the method was not recommended as a substitute.

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Precipitating reductimetry

Organic titrants: Derivatives of aminophenols are among the most effective reducing reagents to be applied titrimetrically. In a series of papers Pollard described their application to both large and small amounts of gold. The earliest procedure[92] was designed primarily for amounts of gold of 5 mg or less, and involved dissolution of gold in small amounts of *aqua regia*, boiling and removal of nitrosyl chloride and chlorine by paraldehyde assisted by air blown through the solution. After dilution of the solution, the gold ion indicator *o*-tolidene was added, followed by silver nitrate as a catalyst, and the titration was carried out with standard "Metol". Except that small amounts of copper could be tolerated, no information was provided concerning the interference of associated metals.

Before the above publication, Pollard[93] in response to a demand for a rapid inexpensive method for "hall marking", developed a titrimetric method for larger amounts of gold. It is surprising that this mercurous titration, a relatively objectionable method, was preferred to the iodide or the iron^{II} reduction, both of which had been recorded more than a decade earlier. While Pollard makes no reference to the earlier methods it is interesting that the proposed procedure involved the iodide reduction. The new method required dissolution in warm *aqua regia*, and the passage of air to eliminate reducing gases. Urea was added to remove nitrous acid, and potassium bromide to accelerate reduction of gold^{I} salt and to form the brown bromoauric acid which was reduced by standard arsenious acid. The latter was made with hydrochloric acid, and contained mercuric chloride and a small amount of potassium iodide. The gold^{III} salt liberated iodine which reacted immediately with the arsenious acid. The reverse reaction, through the action of iodide ion, was prevented by the formation of $HgCl_2.HgI_2$. Furthermore, the iodide concentration was thus kept sufficiently low to prevent interference from other metals except

thallium, palladium and iridium. An amount of the standard arsenic solution almost sufficient to precipitate the gold, as indicated by the disappearance of the brown bromoauric acid, was added. The final trace of the latter was determined by the addition of *o*-tolidene or dianisidine indicator, containing sodium fluoride to complex the iron, and the titration was completed with standard hydroquinone. The results from known gold samples indicated a high degree of accuracy. There was no interference from large amounts of copper, nickel and iron, or from small amounts of lead, zinc, platinum and various other metals. Palladium and ruthenium interfered. The author offers a fair summary of the applicability of the method in that for "hall marking" there would be considerable economy of time and cost as compared to the furnace assay. For general purposes there are objections in that the liquid to be titrated is a mixture with gold and the end-point is thus obscured. Furthermore, two standard solutions are required. In any case the direct titration with arsenic^{III} in a basic medium[80] is simpler and of more general application.

Pollard[94] recorded one of the most useful titrimetric methods for micro amounts of gold. Precipitated gold was dissolved from the filter by bromine water acidified with hydrochloric acid. *Aqua regia* could also be used. Interfering gases were removed by impinging air on the surface of the gold solution. After dilution, the solution was buffered with potassium fluoride, *o*-dianisidine was added, preferably near the end-point, and the gold was titrated with hydroquinone solution. There was no appreciable interference from the associated base metals, copper, silver, iron and nickel. The method was best suited for 2 mg of gold or less; for very small quantities, the gold was initially co-precipitated with tellurium by reduction with sulphur dioxide gas. This precipitation was used successfully for the recovery of gold at a dilution of one part in a thousand million parts of solution. The method was found suitable for the determination of gold in urine. For this determination Jamieson and Watson[95] used a modification of Pollard's method. Samples of urine containing 0·085–0·522 mg of gold were used, and the addition of sodium chloride to assist coagulation and subsequent boiling were required for acceptable recoveries.

Zvyagintsev and co-workers[96,97] used the hydroquinone titration for gold-cyanide solutions. After treatment with nitric acid and potassium chlorate, the solution was adjusted with caustic solution to a slightly acid reaction and then titrated with hydroquinone. The hydroquinone titration was used by Zharkova and Zhaeheva[98] to determine gold in cyanide electrolytes. The solution was neutralised and gold was separated by hydrazine hydrochloride, then redissolved, and finally titrated with hydroquinone in the presence of potassium bifluoride and *o*-dianisidine. The relative value of indicators for the hydroquinone titration was discussed by Belcher and Nutten[99]. Of those examined, 3-methylbenzidine gave the best colour change. End-points with benzidine and 2,7-diaminofluorone were sharper than those obtained with *o*-dianisidine whose change from red-violet to violet was difficult to determine. The authors also discussed the effects of acid strength and time on the colour change of indicators. Milazzo[100] used the hydroquinone titration after a carrier precipitation with copper or lead by hydrogen sulphide or sodium sulphide. The combined sulphides were roasted and the copper selectively removed by sulphuric acid. The gold was dissolved in *aqua regia* and the solution was evaporated with hydrochloric acid to remove oxides of nitrogen. Potassium hydrogen fluoride was added and the gold was titrated with hydroquinone in the presence of *o*-dianisidine. Iridium interfered,

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and under certain conditions the colours of platinum and rhodium salts interfered with the detection of the end-point. The author's claim of superiority over existing methods is not justified. In the present author's opinion the collective precipitation with copper and its subsequent selective dissolution invites greater error than the co-precipitation method with tellurium, proposed by Pollard[94]. Concerning the question of interfering elements, the author has too readily predicted *a priori* the degree of interference from published oxidation-reduction potentials.[101] In any case the description of the experimental results on interferences indicates an inadequate approach.

Various potentiometric titrations have been proposed. Ryabchikov and Knyazheva[102] used a gold wire electrode, in a slightly acid solution of gold freed from nitric acid by evaporation with hydrochloric acid, and titrated the hot solution with hydroquinone or Mohr's salt in a current of carbon dioxide. Of the platinum group only iridium interfered. Czaplinski and Trokowicz[103] used platinum and calomel electrodes with a similarly treated gold solution, and titrated at a pH of 2–5 with a 0·01*N* hydroquinone solution. The potential change at 50°, at the equivalence point, after adding one drop of the titrant, was above 100 mV. Copper and platinum did not interfere. Reishakhrit and Sukhobokova[104] used a rotating platinum electrode and 2*N* sulphuric acid as an auxiliary electrolyte. The hydroquinone titration was carried out at 60° at a potential of 1 volt in relation to a standard calomel electrode. Palladium did not interfere.

Ascorbic acid has proved to be a useful titrant for gold. Stathis and Gatos[105] used an excess of the standard reagent, and a gold solution containing hydrochloric acid but free of oxidising constituents, and titrated the excess with iodine solution. The results were excellent, and copper did not interfere. No references were made to other interferences. Erdey and Rady[106] developed a potentiometric method with ascorbic acid as the titrant. The gold^{III} solution was maintained at 50°, the acidity at pH 1·6–3, and the chloride concentration at a maximum of 0·1*N*. The end-point was readily discernible, and the accuracy of the method was about $\pm 1\%$ with 0·01*N* solutions. There was no interference from mercury^{II}, copper^{II} or iron.^{III} Platinum^{IV} caused high results. Both ascorbic acid methods are recommended.

Hydrazine sulphate has also been used for the potentiometric determination of as little as 0·1 mg of gold in 0·01–0·001*M* hydrochloric acid.[107] Franceschi[108] used potassium oxalate to precipitate gold and back-titrated the excess with potassium permanganate.

Reduction by metal salts: The very early titrimetric methods included reduction of gold^{III} salts to gold by standard iron^{II} salts, and back-titrations with potassium permanganate. Thus in 1878, Juptner[109] determined gold in alloys after dissolution in *aqua regia* and boiling to remove oxidising gases.

In 1913, French[110] discussed the new titrimetric methods recently introduced into Mints. One procedure involved the determination of gold by reduction with Mohr's salt in sulphuric acid solution, and titration of the excess with potassium permanganate. Tsobar[111] used the method for gold alloys containing copper. The hydrochloric acid solution, free of oxides of nitrogen, was neutralised with sodium hydrogen carbonate to the formation of an amorphous precipitate. It was then slightly acidified with sulphuric acid and titrated with potassium permanganate. The method remains one of the most acceptable for the titrimetric determination of gold, and appropriate

procedures are recorded in modern textbooks.[78] Iron^{II} reduction has also been used, the end-point being indicated potentiometrically. Moller and Weisbrod[112–114] have thus determined gold from both a hydrochloric acid and a nitric acid medium. To ensure complete conversion to gold^{III}, chlorine was added, in which case only the second inflection corresponded to the reduction of the gold salt. In the presence of nitric acid[112,114] the latter inflection was less abrupt, but the addition of alcohol and potassium sulphate provided some improvement. Platinum and palladium interfered.

Titanium^{III} chloride has also been used for the potentiometric determination of gold. As compared with iron^{II} salts, there is the disadvantage of relative instability in air. Zintl and co-workers[115–117] used a hydrochloric acid solution and potassium bromate to ensure oxidation of gold^{I} salts. Zintl[118] also provided a potentiometric titration with chromium^{II} chloride. Tervalent gold, bivalent copper and univalent mercury could be titrated in succession. The gold was dissolved in 2–5% hydrochloric acid, and bismuth chloride was added as a catalyst. Gold salts alone produced high results through the catalytic decomposition of chromium chloride by metallic gold. This was prevented by copper ion.

Vanadyl sulphate has also been used for potentiometric titrations. Del Fresno and Mairlot[119] used strongly alkaline gold solutions above 50°.

Muller and Tanzler[120] used copper^{I} chloride, whose stability was acceptable if air was excluded. Chlorine was added to ensure complete conversion to $AuCl_4^-$, which was reduced by copper^{I} to gold. Solutions containing both platinum^{IV} and gold^{III} could be titrated. Lingane[121] developed a coulometric titration of gold, in which the $CuCl_2^-$ was generated electrolytically from a supporting electrolyte of 0·04*M* copper^{II} sulphate in 1–2*M* hydrochloric acid solution, with a generator cathode of pure gold and a generator anode of cadmium metal in an anolyte of cadmium chloride in potassium chloride. Air was removed by a current of nitrogen, and the equivalence-point was detected potentiometrically with gold-saturated calomel electrodes. Gold was reduced stepwise first to $AuCl_2^-$, then to gold. There was some evidence that nitrate ion at a concentration of 0·02*M* did not interfere. Thus it would seem that the author need not have evaporated the gold solutions with hydrochloric acid. Samples of gold in the range of 1 to 100 mg were titrated with an average error of ±0·3%. It is significant that there exists the possibility of titrating 100 micrograms of gold within an error of ±1%. A large amount of platinum, more than half that of the gold, produced positive errors; small amounts were without effect. Large amounts of copper, silver, mercury and lead did not interfere. The author's statement that "since lead does not interfere, the titration is applicable to the lead-gold alloy obtained by fire assay methods, provided platinum group metals are not present" is unacceptable. Aside from the fact that almost any classical method for a metal can be made applicable irrespective of the associated metals, the author's claim makes no recognition of the fact that the dissolution and preparation for the proposed coulometric titration of a 25-g lead button containing a milligram or so of gold would be no simple procedure. Furthermore, if the lead is removed by cupellation, it is unlikely that an experienced chemist would choose lengthy procedures when simple weighing is sufficient. The proposed coulometric method can be useful for specific purposes, but it is not recommended for general use.

With the exception of iron^{II} none of the transition metals' salts is recommended as titrants; most of them lack stability in air and all of them involve amperometric or

potentiometric techniques. This objection applies also to the tin^{II} reduction. Muller and co-workers[122,123] have used this method for gold and platinum, in an atmosphere of nitrogen. When both of these metals are present the one end-point represents complete precipitation of both metals. Tin^{II} chloride was also used by Hirano[124] as a titrant, with the end-point indicated photometrically. A clear break in the developing purple colour appeared, provided that the acidity of the solution was kept below 0·05*N* and excess chlorine was present. There was no interference from small amounts of copper, lead and iron. Because so many simpler methods are available this technique has little to recommend it. An interesting coulometric method involving electrogenerated tin^{II} was described by Baird and Lingane.[125] The optimum supporting electrolyte was 3–4*M* sodium bromide, 0·3*N* hydrochloric acid and 0·2*M* tin^{IV} chloride. A gold generator cathode was used. The solution was de-aerated with nitrogen. The reduction proceeded from $AuBr_4^{2-}$ to gold. The end-point could be observed amperometrically through the use of two small, identical, gold electrodes maintained at 100 to 200 mV. The titration could also be followed spectrophotometrically at a wavelength of 400 mμ. In contrast to the amperometric and potentiometric methods, the spectrophotometric procedure indicated only the reduction to $AuBr_2^-$. With the first two methods, and 0·5–23 mg of gold, the average error was $\pm$0·3%. With the last the average error was about 2%. Interference from other metals was not investigated.

A unique titrimetric method for the determination of colloidal gold involves a titration with standard potassium cyanide. Wagner[126] used an adaptation of the method for the determination of gold in cyanide solution. The latter was evaporated to fumes with sulphuric acid to produce metallic gold, which, after dissolution in *aqua regia*, was treated with ammonia. Standard potassium cyanide was added, and the excess over that required to dissolve the gold precipitate was titrated with silver nitrate, with potassium iodide as an indicator. For the direct determination of gold sols produced by a variety of methods, Pennycuick and Woolcock[127] used a standard potassium cyanide solution. At a pH above 7, 8 moles of potassium cyanide reacted with 2 formula weights of gold.

A direct determination of gold by titration with 0·1*N* sodium arsenite was developed by Szebelledy and Viczian.[128] The chloride solution was treated with sodium bromide, and the red $AuBr_4^-$ ion was titrated at 90° in the presence of gelatin, which prevented reduction to metallic gold. The arsenite reduced the red auric bromide to colourless $AuBr_2^-$. The method suffers from a large variety of metal interferences, and the end-point is not obtained without some difficulty. Better methods are available. In the author's opinion this statement also applies to certain of the titrimetric methods proposed by Lenher.[81] These procedures require the reduction by a standard sulphur dioxide solution of $gold^{III}$ chloride containing magnesium chloride and potassium bromide, or magnesium chloride alone, or sodium chloride. The author quotes very acceptable results, but in this case there is the problem not only of interferences and uncertain end-points, but also of the instability of the reducing reagent. It is interesting to note that whereas the titration results in a reduction to univalent gold, the reagent sulphur dioxide is used satisfactorily as a precipitant for gold. As far as the present author knows, little has been recorded concerning the interference of alkali metal and alkaline earth salts with the precipitation of gold by sulphur dioxide.

Methods for gold have been included in the large number of heterometric titrations

developed by Bobtelsky[129] and associates. To determine gold alone, the method recommended involves the titration with nitron of a solution containing about 1 mg of gold, potassium thiocyanate and either dilute or concentrated ammonia. With the former the white compound AuN appeared, and with the latter the yellow Au_2N_3 was formed. Procedures were provided for determining gold in mixtures of palladium and platinum. The titration required 5–10 minutes and the error was between 0 and 1%. The publication quoted contains informative material, potentially useful in both titrimetric and gravimetric areas.

Zusammenfassung—Die Ubersicht enthält die einschlägige Literatur bis Juli 1960. Es wurde versucht die im allgemeinsten anwendbaren titrimetrischen und gravimetrischen Methoden zur Bestimmung von Gold herauszufinden. Wenngleich einige Methoden unter diesem Gesichtpunkte abgelehnt werden mussten, soll zugegeben werden, dass sie unter Bedingungen, wo zahlreiche Proben zu analysieren sind und einigermassen konstante Bedingungen vorwalten, von grossem Nutzen sein können. Wegen ihrer weiten Anwendbarkeit wird die Methode, Gold aus cyanidhaltiger Lösung zu fällen, separat behandelt. Die zahlreichen Widersprüche, betreffend die iodometrische Methode der Goldbestimmung wurden betont.

Résumé—Cette étude comprend toute la littérature appropriée publiée avant juillet 1960. L'auteur a essayé d'identifier les méthodes titrimétriques et gravimétriques les plus généralement applicables pour le dosage de l'or. Alors que certaines méthodes ont été rejetées pour cette raison, on admet que si de nombreux dosages sont faits et que les compositions qualitatives sont à peu près constantes, certaines de ces méthodes peuvent être particulièrement efficaces. A cause de son application étendue, la précipitation de l'or en solution de cyanure est traitée séparément. Le caractère controversé de la méthode iodométrique pour l'or a été souligné.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—V*

THE DETERMINATION OF CADMIUM

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Summary—A method is described for the determination of cadmium in beryllium or beryllium oxide. Cadmium is precipitated with benzotriazole using nickel as a carrier. A further separation from other elements is made by passing a chloride solution through Dowex-1 anion-exchange resin. The cadmium is finally determined with dithizone. The method is accurate to ±5% or 0·4 μg of cadmium, whichever is greater. No interference is caused by the presence of 10-mg amounts of 68 elements.

INTRODUCTION

A METHOD for the determination of cadmium in beryllium or beryllium oxide is presented which is specific within the limits investigated. No interference is caused by at least 10-mg amounts of 68 elements. The presence of greater than 100 μg of zinc necessitates a minor modification of the method. The presence of zinc in greatly interfering amounts can be recognised by the red colour of the aqueous phase during the dithizone-chloroform extraction.

The method is based on the precipitation of cadmium from an ammoniacal citrate solution with benzotriazole, using nickel as a collector.[1] A 10% hydrochloric acid solution containing cadmium and other elements precipitated with benzotriazole (zinc, copper, cobalt and nickel) is passed through a column containing Dowex-1 anion-exchange resin. Cadmium and zinc are retained by the resin and are subsequently eluted with 3*M* nitric acid. Cadmium is then extracted from a strongly alkaline medium with a chloroform solution of dithizone.[2] The absorbance of this extract measured at 518 mμ is a linear function of the cadmium concentration, at least between 0·05 and 1·0 μg of cadmium per ml. The colour is stable in diffuse light for at least 24 hours.

EXPERIMENTAL

Apparatus

Beckman DU spectrophotometer: With 1-, 2- and 5-cm cells.

Ion-Exchange columns: 1 cm I.D., 12 cm long, containing 8 cm of Dowex-1, 200–400 mesh, 8% crosslinkage.

Reagents

Distilled water was used throughout.

Standard cadmium solution: Dissolve 100 mg of pure cadmium metal in 1 ml of nitric acid. Add 1 ml of sulphuric acid and evaporate to near dryness. Cool and dilute to 1 litre. Dilute this solution to obtain a solution containing 1 μg of cadmium per ml.

* Part IV: *Talanta*, 1960, **5**, 250.

Nickel solution: Dissolve sufficient nickel chloride, nitrate, or sulphate to obtain a solution containing 5 mg of nickel per ml.

Nitric acid, 16*M* and 3*M*.

Citric acid, 50% (w/v).

Sulphuric acid, 18*M*.

Benzotriazole, 2% (w/v) aqueous solution: Prepare fresh solution by adding hot water to a weighed amount of the solid material.

Ammonium hydroxide, 12*M*.

Perchloric acid, 70%.

Hydrochloric acid, 12*M* and 1·2*M*.

Tartaric acid, 2% (w/v).

Hydroxylamine hydrochloride, 5% (w/v).

Sodium hydroxide, 40% (w/v), containing 0·05% (w/v) potassium cyanide.

Dithizone solution, 10–15 mg in 1 litre of chloroform: Purify the dithizone solution in the usual manner,[3] and adjust the dithizone concentration by appropriate dilution of the purified material, using the reported molar absorptivity, 41,500 at 605 mμ.[4]

Procedure

Transfer a sample containing approximately 10 μg of cadmium to a 600-ml beaker. Dissolve beryllium oxide in hot 6*M* sulphuric acid (20 ml per g of oxide). Dissolve beryllium metal by suspending the sample in water and gradually adding hydrochloric acid (10 ml per g of metal). When the reaction ceases, add a few drops of 30% hydrogen peroxide if necessary, to dissolve any remaining particles of unoxidised metal. Heat to destroy the excess peroxide.

If the sample was dissolved in 6*M* sulphuric acid, add 10 ml of hydrochloric acid. If the sample was dissolved in hydrochloric acid, add 20 ml of 6*M* sulphuric acid. Dilute to about 150 ml with water, add 5 ml of the nickel solution and sufficient 50% citric acid to complex the beryllium (25 ml per g of beryllium), and adjust the pH to 8·25 ± 0·1 with ammonium hydroxide. Dilute to about 300 ml with water. Add 25 ml of 2% benzotriazole solution and digest on a steam bath for 2 hr. Allow the precipitate to stand overnight at room temperature. Add filter pulp, filter through Whatman-40 filter paper, and wash with a minimum amount of a 1% ammonium citrate solution previously adjusted to pH 8·25.

Transfer the paper to the original beaker, add 25 ml each of nitric acid and perchloric acid, evaporate to fumes of perchloric acid and finally to dryness.

Dissolve the salts in 100 ml of 1·2*M* hydrochloric acid, warming if necessary, and cool to room temperature. Pass this solution through the anion-exchange resin (which has previously been washed with 100 ml of 3*M* nitric acid, then 100 ml of water, and finally, converted to the chloride form with 100 ml of 1·2*M* hydrochloric acid) and wash the resin with about 10 column volumes (about 200 ml) of the same acid, discarding the eluate.

Elute the cadmium by passing 125 ml of 3*M* nitric acid through the column. Add to the eluate 1 ml of sulphuric acid and evaporate to dryness. Dissolve the salts in water.

Transfer the solution, or an aliquot containing a maximum of 10 μg of cadmium, to a 125-ml separatory funnel. Add in the following order, swirling after each addition, 25 ml of 2% tartaric acid, 1 ml of 5% hydroxylamine hydrochloride, 5 ml of 40% sodium hydroxide−0·05% potassium cyanide solution and 20 ml of dithizone solution. Shake for 1 min, insert a little cotton in the stem of the funnel and filter the chloroform layer into a 1-, 2- or 5-cm cell. Measure the absorbance of the pink extract at 518 mμ, using chloroform as a reference. Determine the cadmium concentration by reference to a standard curve obtained by carrying known amounts of cadmium through the dithizone extraction procedure. A blank and at least one standard should be carried through the entire procedure.

Precipitation of nickel with benzotriazole and collection of cadmium

Precipitation of copper with benzotriazole is carried out at a pH of 7·0–8·5.[2] Iron^{II}, silver, nickel, cadmium, zinc and cobalt ions give similar precipitates, but the optimum pH for precipitation is not given. In our investigation we attempted to ascertain the optimum pH for quantitative recovery of cadmium as the benzotriazole compound by co-precipitation with nickel. Table I indicates that cadmium is quantitatively recovered at a pH of 8·0–8·5.

The experiments described in Table I were an attempt to determine the optimum pH for precipitation under several conditions. The effect of beryllium oxide, sulphuric acid, and citric acid was investigated at several pH values.

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The table is self-explanatory, indicating that at a pH of 7·5 reasonably good recovery of cadmium is obtained from a water solution, whereas the presence of sulphuric acid leads to slightly low results. The presence of citric acid leads to very low results. However, the presence of beryllium, which forms a complex with citrate, leads to much better recovery. Excellent results are obtained under all of the conditions tested at a pH of 8·0 to 8·5. Consequently, a pH of 8·25 is recommended.

Table 1.—Recovery of cadmium by co-precipitation with nickel[a]

BeO, *g*	H_2SO_4, mmoles	Citric acid, *g*	pH	Cd recovered, %	BeO, *g*	H_2SO_4, *mmoles*	Citric acid, *g*	pH	Cd recovered, %
0	240	20	7·5	54,72	1·0	300	20	8·0	98,99
0	120	0	7·5	91,92	1·0	120	10	8·0	102
0	240	0	7·5	90	1·5	330	20	8·0	99
0	360	0	7·5	88,92	2·0	360	20	8·0	100,98
0	0	0	7·5	93	2·0	240	20	8·0	105
0·5	270	20	7·5	58,29	0	240	20	8·25	99,97
0·5	60	5	7·5	98	1·0	300	20	8·25	100,100
1·0	300	20	7·5	78,80	0	240	20	8·5	99
1·0	120	10	7·5	104	0·5	270	20	8·5	99
1·5	330	20	7·5	95	1·0	300	20	8·5	101,101
2·0	360	20	7·5	99,99	1·5	330	20	8·5	101
2·0	240	20	7·5	100	2·0	360	20	8·5	100
0	240	20	8·0	100,98	0	240	20	9·0	99,100
0	0	0	8·0	101	0·5	270	20	9·0	92,97
0·5	270	20	8·0	99	1·0	300	20	9·0	93,95
0·5	60	5	8·0	101	1·5	330	20	9·0	98
					2·0	360	20	9·0	96,98

[a] 12·5 μg of cadmium added. Ten ml of 12*M* HCl present in all cases

Extraction and measurement of the cadmium-dithizonate complex

The amount of dithizone specified in the above procedure is adequate for up to 24 μg of cadmium. If the absorbance of the sample indicates a higher cadmium content, a smaller aliquot of the sample solution is recommended. If no more sample solution is available, a second, and, if necessary a third extraction with fresh portions of dithizone should be made and the chloroform solution treated as described for the separation of cadmium from excessive amounts of zinc.

The colour of the cadmium dithizonate is stable in diffuse light for at least 1 day. The absorbance is a linear function of concentration, at least up to 1·0 μg of cadmium per ml. The absorbance of 12·1 μg of cadmium per 20 ml of chloroform-dithizone solution is approximately 0·44 when 1-cm cells are used. Inasmuch as the Lambert (Bougher) Law is obeyed, a similar absorbance is obtained from 2·42 μg of cadmium when 5-cm cells are used.

Effect of other elements

In testing the effect of other elements on the determination of cadmium by the procedure described, the elements were added to solutions containing the appropriate amounts of beryllium sulphate, sulphuric and hydrochloric acids before the precipitation with benzotriazole.

No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, As^{III}, Ba, Bi, B, Br, Ca, Ce^{IV}, Cs, Cr^{III}, Co, Cu^{II}, Dy, Er, Eu, F, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Hg^{II}, Mo^{VI}, Nd, Ni, Nb, Pd^{IV}, P(as PO_4^{3-}), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Na, Sr, Ta, Te^{IV}, Tb, Tl^{I}, Th, Tm, Sn^{II}, Ti^{III}, W^{VI}, U^{VI}, V^{V}, Yb, Y, or Zr or 100 μg of zinc. The interference of larger amounts of zinc may be eliminated as described later.

It should be noted that the preliminary precipitation with benzotriazole separates cadmium from all but the following elements: zinc, cobalt, copper, nickel and silver (if present, silver should be removed as silver chloride). The subsequent anion-exchange step provides a solution containing only cadmium and zinc.

If the preliminary benzotriazole precipitation step is omitted and chloride solutions of the sample containing 10 mg of the above listed elements are passed directly through the anion-exchange columns, results are within the stated accuracy limits with the following limitations:

(1) Thallium is adsorbed by the resin in a chloride medium and will strongly interfere with the final cadmium determination unless additional remedial steps are taken.

(2) Mercury is also adsorbed by the resin and is only incompletely removed by evaporating the sulphuric acid solution to dryness.

(3) Platinum, palladium, iridium and rhodium are retained by the resin. They largely remain on the column when the cadmium is eluted, and tend to make the columns useless for further analytical purposes.

(4) Gold is also retained by the resin and its removal is difficult.

(5) Lead quantitatively accompanies the cadmium. Its interference is almost identical to that described for zinc and can be obviated in the same manner.

Effect of zinc

If more than 100 μg of zinc are present in the aliquot, some of the dithizone is consumed to convert a small portion of the zinc in the aqueous layer to a dithizone compound. The aqueous layer is then coloured red (depending, of course, on the amount of zinc present) and more dithizone is needed to extract the cadmium. The presence of zinc in interfering amounts may be ascertained by making a second dithizone extraction of the aqueous phase. A pink colour indicates either zinc or cadmium. In this case proceed as follows:

Extract twice with 20 ml of dithizone solution, combining the extracts in another separatory funnel. Revert the cadmium by extracting the chloroform phase with 20 ml of 6*M* sulphuric acid. Evaporate the aqueous phase to dryness, dissolve the salts, and extract the cadmium as described in the procedure. The interference of up to 10 mg of zinc may be eliminated in this manner. An alternative method of separating cadmium and zinc, which has been successfully used for the determination of cadmium in 1-g samples of zinc, is by a cation-exchange separation from 0·3*M* hydriodic acid −0·075M sulphuric acid. Cadmium forms an iodide complex which is not retained on a cation resin whereas zinc is adsorbed.[5]

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APPLICATION OF THE METHOD

A sample of beryllium oxide analysed for cadmium using this procedure was found to contain less than 0·1 ppm of cadmium. The recovery of cadmium added to this sample of beryllium oxide is shown in Table II.

TABLE II. RECOVERY OF CADMIUM ADDED TO BERYLLIUM OXIDE

BeO, *g*	Cd added, μg	Cd found μg
1	3·0	3·3[a]
1	8·0	7·6
3	1·0	1·2[a]
5	0·5	0·25[a]
1	10·0	10·4
1	25·0	23·8
1	50·0	51·9
1	100·0	97·3
2	100·0	103·5

[a] 5-cm cells used. 1-cm cells used for other determinations.

Blank values corresponding to 0·02 μg of cadmium were obtained with the amounts of reagents used during the analysis.

Results obtained when the method was applied to New Brunswick Laboratory standard samples of beryllium oxide are shown in Table III.

TABLE III. ANALYSIS OF NBL STANDARDS

Sample[a]		Cd found, μg			Nominal Value
Be	85	0·41,	0·47		
	86	0·48,	0·46		
	87	0·47,	0·47		
	88	0·40,	0·44		
BeO	72-1	2·1,	2·2,	2·1[b]	2·16
	72-2	1·2,	1·2		0·72[c]
	72-3	0·8,	0·8		0·36[c]
	72-4	0·7,	0·7		0·18[c]
	72-5	0·45,	0·50		?

[a] 2-g samples were taken for the above determinations. 5-cm cells were used for absorbance measurements.

[b] The results in this table were obtained at Ledoux. Sample 72-1, analysed at General Electric Company was found to contain 1·9, 2·0, and 2·0 ppm of cadmium.

[c] Based upon amount added to 72·5.

Zusammenfassung—Eine Methode zur Bestimmung von Cadmium in Beryllium und Berylliumoxyd wird beschrieben. Unter Verwendung von Nickel als Träger wird Cadmium mit Benzotriazol gefällt. Zur Abtrennung weiterer Metalle wird die chloridlösung durch einen Anionenaustauscher (Dowex-1) Die Methode ist auf $\pm 3\%$ oder 0·3 μg genau, was immer grösser ist. Keine Störungen werden verursacht durch Anwesenheit von 10-mg Mengen von 68 anderen Elementen.

Résumé—Les auteurs décrivent une méthode de dosage du cadmium dans le beryllium ou l'oxyde de beryllium. Le cadmium est précipité par du benzotriazole en utilisant du nickel comme entraîneur. Une séparation ultérieure des autres éléments est faite en faisant passer une solution de chlorure sur une résine Dowex 1 échangeuse d'anions. Le cadmium est dosé finalement par la dithizone. La précision de la méthode est ± 3 pour cent ou 0,3 μg de cadmium. La présence de 68 éléments en quantité de 10 mg ne gêne pas le dosage.

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TETRACYANOETHYLENE CHEMISTRY

INDIRECT PHOTOMETRIC DETERMINATION OF ANTHRACENE IN NAPHTHALENE

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Summary—Anthracene can be determined in naphthalene indirectly by measuring the destruction of the colour of a naphthalene-tetracyanoethylene (TCNE) complex after anthracene and TCNE have reacted via the Diels-Alder reaction. A trace analysis method of indirect spectrophotometry can be used to extend the determination to as low as 0·01% (5×10^{-5} *M*) of anthracene in the final solution in a ten thousand-fold excess of naphthalene. Pentamethylbenzene can be used instead of naphthalene but it is a less desirable reagent. Various possible interferences have been studied.

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INTRODUCTION

UNTIL recently there were available few simple colorimetric methods for detection or determination of anthracene or other aromatic hydrocarbons. Novel methods have been developed for the detection of anthracene and other hydrocarbons using piperonal chloride and benzal chloride,[1,2] isatin,[3] and 3-nitro-4-dimethylaminobenzaldehyde.[4]

In addition, ultraviolet spectrophotometry following chromatographic separation on alumina[5] has been applied to the determination of anthracene and other polynuclear aromatic hydrocarbons. Anthracene has also been determined fluorimetrically.[6]

Apparently no colorimetric methods have utilised the Diels-Alder reaction of anthracene. Extensive studies of tetracyanoethylene (TCNE) and its coloured complexes with aromatic hydrocarbons[7] suggested a simple indirect colorimetric method for anthracene. Advantage was taken of the rapid and quantitative Diels-Alder reaction of TCNE with anthracene at room temperature[8] in contrast to maleic anhydride which reacts rapidly at reflux temperature with anthracene,[9] but only slowly at room temperature.[10]

The pertinent data on the coloured π-complexes of TCNE, as summarised in Table I, suggested a colorimetric measurement of anthracene based on the destruction of the colour of a complex of TCNE and excess naphthalene:

$$\underset{\text{(red complex)}}{C_{10}H_8(TCNE)} + C_{14}H_{10} \rightarrow C_{10}H_8 + \underset{\text{(colourless adduct)}}{C_{14}H_{10}{-}TCNE}$$

These coloured complexes have been utilised in paper chromatography.[11]

Naphthalene was selected to form the coloured complex since it is frequently found in large amounts in mixtures of aromatic compounds, is quite soluble in chloroform,

TABLE I.—π-COMPLEXES OF TCNE AND AROMATIC HYDROCARBONS

Aromatic Hydrocarbon	K	$\lambda_{max}, m\mu$	ε
Cyclohexene	0·247	422	4760
Benzene	2·0	384	3570
Toluene	3·7	406	3330
Naphthalene	11·7	550	1240*
Pyridine	12·0	421	10500*
Fluorene	18·0	570	1430*
Pyrene	29·5	724	1137*
Pentamethylbenzene	123·0	520	3270

* Second absorption maximum omitted

does not complex the TCNE too strongly, and has an absorption maximum well removed from the 400-mμ region in which some aromatics absorb strongly.

EXPERIMENTAL

Reagents

Tetracyanoethylene (TCNE) was kindly supplied by the Central Research Department, Experimental Station, E. I. duPont de Nemours and Company, or was synthesised.[12] It was purified to a white powder by sublimation.

Anthracene was recrystallised four times from diethyl ether. Sublimed naphthalene, pentamethylbenzene, and other materials were used as received. Cyclopentadiene was prepared by cracking dicyclopentadiene at 160° and taking the middle fraction of cyclopentadiene distilling at 40°.

Chloroform and methylene chloride were of reagent grade.

TCNE reagent, naphthalene, 0·75M trace analysis solution: Dissolve 12·8 mg of TCNE in 15 ml of methylene chloride and add 9·6 g of naphthalene. Dilute with 50 ml of chloroform prior to the addition of the sample. For the pure chromogenic reagent, dilute to exactly 100 ml with chloroform; this reagent had an absorbance of about 0·9 on the Bausch and Lomb Spectronic 20 Colorimeter.

TCNE reagent, naphthalene, 0·05–0·50M solutions: Dissolve 51·2 mg of TCNE in 15 ml of methylene chloride, or in 1 ml of triethyl phosphate or dimethoxyethane. Add 0·64 to 6·4 g of naphthalene for the desired molarity. Dilute with 50 ml of chloroform before the addition of the sample. See Table IV for the stability of 0·25M naphthalene reagent.

TCNE reagent, pentamethylbenzene, 0·10M: Prepare as above using 5·1 mg of TCNE and 1·48 g of pentamethylbenzene instead of naphthalene.

Procedures

(*a*) Anthracene, 0·5–5 $\times$ $10^{-4}M$ (final solution): Add a 10- or 25-ml aliquot, containing 0·9 to 9 mg of anthracene in chloroform or alkane solvent, to the 0·75M naphthalene trace analysis reagent; dilute to exactly 100 ml with chloroform. After 40 min at room temperature, measure at 550 mμ according to Method C.[13] Set the instrument to read 0% transmission in the darkness and 100% transmission with the *sample solution* in the light path, then read the % transmission or absorbance with the pure chromogenic reagent in the light path. The last two operations obviously must be performed for each sample and for each point on a calibration curve covering the 0·5 to 5 $\times$ $10^{-4}M$ anthracene concentration range (see Fig. 2).

(*b*) Anthracene, 0·3–3·9 $\times$ $10^{-3}M$ (final solution): Add a 10- or 25-ml aliquot, containing 5·3 to 70 mg of anthracene in chloroform or alkane solvent, to the 0·05M naphthalene reagent; dilute to exactly 100 ml with chloroform. After 40 min at room temperature, measure at 550 mμ. Prepare a calibration curve for this range as shown in Fig. 1.

If naphthalene is present in the sample, add only sufficient naphthalene to the reagent to bring the final concentration to 0·05M. If no interferences are present, mix the sample and TCNE before adding naphthalene, to reduce the reaction time.

Anthracene in the 1·5 to 3·5 $\times$ $10^{-4}M$ range in the final solution may be determined similarly using 0·1M pentamethylbenzene reagent, a reaction time of 2 to 4 hr, and a wavelength of 520 mμ.

(*c*) Anthracene in cyclopentadiene: Add an excess of maleic anhydride of no more than 0·4 g to the sample at room temperature and allow it to react with the cyclopentadiene for 2 to 3 hr. The presence of the yellow maleic anhydride-anthracene complex[14] after that time indicates that excess anhydride is present. Follow procedures (*a*) or (*b*) for the determination of anthracene.

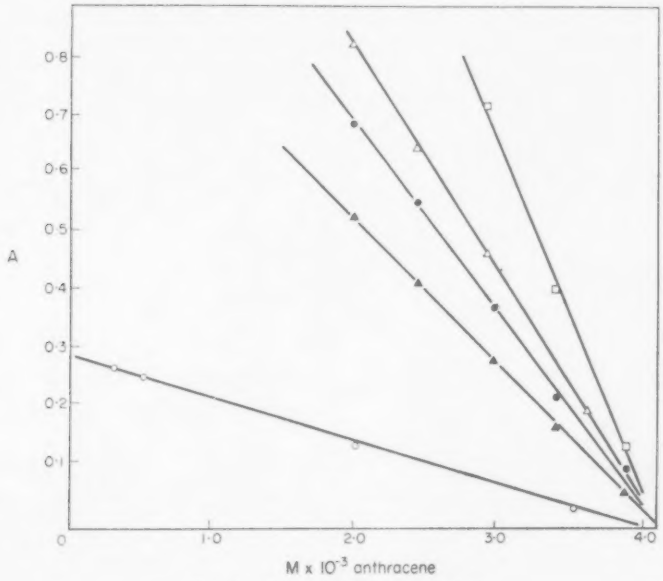

FIG. 1.—Initial TCNE 4 $\times$ $10^{-3}M$
Naphthalene: 0·05M ○
0·15M ▲
0·20M ●
0·25M △
0·50M □

DISCUSSION OF RESULTS

Fig. 1 shows various calibration curves of absorbance versus concentration of anthracene using naphthalene–TCNE reagents. These curves show conformity to Beer's Law up to about 3·9 $\times$ $10^{-3}M$ anthracene. The absorbance is not zero when the stoichiometric amount of anthracene has been added to the TCNE. The anthracene may not have been 100% pure or it may be that the equilibrium is not favourable in this concentration range.[13] The last traces of TCNE are complexed by a proportionately large concentration of naphthalene. Although the 0·05M naphthalene reagent gives a satisfactory range in procedure (*b*), 0·10 or 0·15M reagents may be used for greater sensitivity and only a slightly smaller range.

One advantage of using naphthalene is that its relatively small stability constant (see Table 1) permits a variation in the concentration of naphthalene, and a concomitant variation in the sensitivity of the method, without retarding the Diels-Alder reaction appreciably. A second advantage is, that if a large amount of naphthalene is present with the anthracene, it can be used to form the coloured complex. Thus, in general, a large amount of an interfering aromatic hydrocarbon need not be

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an interference, but it can be used to form the coloured aromatic–TCNE complex for the analysis. This method serves as a model system for the determination of other Diels–Alder aromatic dienes.

Unfortunately, at high concentrations of naphthalene, concentrations of anthracene below $3 \times 10^{-3}M$ cannot be measured without resorting to the trace analysis method described below. Also, the actual molar absorptivity as shown in Table 1 is not approached, it being 58 for $0{\cdot}05M$ and 540 for $0{\cdot}50M$ naphthalene.

To make analytical use of the favourable slope of the calibration curve for $0{\cdot}75M$ naphthalene, trace analysis Method C[13] is used to extend the analysis to the $10^{-5}M$ range. This method yields a plot in which absorbance increases with increasing concentration of anthracene as shown in Fig. 2.

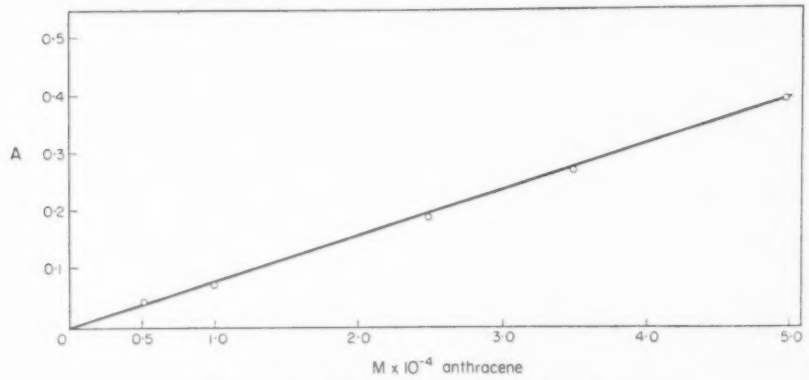

FIG. 2.—Naphthalene $0{\cdot}75M$: Initial TCNE $1 \times 10^{-3}M$

In this method, the extremely sensitive $0{\cdot}75M$ naphthalene reagent is used to obtain readings at the more accurately read section of the absorbance scale. In ordinary indirect methods, a low concentration of anthracene would give high absorbance readings, which are less accurately read.

TABLE II.—DETERMINATION OF ANTHRACENE

Procedure	Interference	Anthracene	
		Present, *mg*	Found, *mg*
(*a*)	None	0·91	1·07
(*a*)	None	1·82	1·71
(*b*)	$0{\cdot}23M$ benzene	36·4	34·5
(*b*)	$0{\cdot}23M$ benzene	52·8	53·5
(*b*)	$0{\cdot}188M$ toluene	52·8	54·0
(*b*)	$0{\cdot}188M$ toluene	71·0	71·0

Thus, this is the recommended method for determining small amounts of anthracene. It compares favourably with the sensitivity of the ultraviolet absorption bands of anthracene in the 375-mμ region.

Table II contains results obtained in the determination of anthracene by both procedure (*a*) and procedure (*b*).

Using the pentamethylbenzene reagent lowers the range of the analysis to $10^{-4}M$ since pentamethylbenzene forms a complex ten times stronger than naphthalene, as shown in Table I. One disadvantage is that the calibration curve fails to follow Beer's Law at concentrations of anthracene approaching the stoichiometric point. In addition, the absorbance is not constant until after a reaction time of 2 to 4 hr, as shown in Table II. These factors make it undesirable to increase the concentration of pentamethylbenzene to match the sensitivity of the 0·50 to 0·75M naphthalene curves. Hence this reagent is not recommended where the naphthalene reagent can be used.

TABLE III.—TIME STUDY OF $4 \times 10^{-4}M$ TCNE-0·1M PENTAMETHYLBENZENE AT VARIOUS ANTHRACENE CONCENTRATIONS

Time, *hr*	% Transmittance			
	2·0	2·9	3·4	3·9
	($\times 10^{-4}M$) anthracene			
1	45	63	70	75
2	47	68·5	80	81·5
4	47	71	85	86
4 days	47	75	93	92

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The results in Table IV demonstrate the stability of the naphthalene–TCNE complex after reaction with varying amounts of anthracene. This appears to rule out appreciable alkylation of naphthalene at room temperature similar to the alkylation of phenanthrene.[15]

TABLE IV.—STUDY OF STABILITY OF TCNE COMPLEXES

Time	$4 \times 10^{-3}M$ TCNE, 0·25M naphthalene			$2 \times 10^{-3}M$ TCNE, 0·0125M pentamethylbenzene, $1{\cdot}95 \times 10^{-3}M$ anthracene
	2·0	2·9	3·9	
	($\times 10^{-3}M$) anthracene			
40 min	14·5%	36·5%	85·0%	88·5%
1 month	14·0	37·0	86·0	89·5
4 months				89·5
5 months	14·0	37·5	87·0	
6 months*				93·0
7 months*	14·0	37·0	79·0	

* Taken out of hood and left in sunlight

The constant absorbance of such solutions after 5 to 7 months indicates that the complex may be prepared in advance and used when desired. The change in absorbance of one of the solutions from the 5th month to the 7th month may possibly be attributed to putting the solutions in the sunlight. It is recommended to store the reagents in a cool dark place such as a hood.

Such a constant absorbance also demonstrates that the Diels-Alder reaction is essentially complete and that there is no measurable reverse Diels-Alder reaction taking place.

INTERFERENCES

Table V summarises the interference tested on the TCNE-naphthalene complex. The possible interferences are alkenes, aromatic or alkyl dienes, substituted benzenes, polynuclear aromatic hydrocarbons, phenols, amines, alcohols, water, and thiols.

In general, it can be predicted from Table 1 that substances with a small stability constant relative to naphthalene will not interfere and *vice versa*. Thus, large amounts of alkenes like cyclohexane should not interfere. Likewise, large amounts of benzene and toluene should not interfere, and this is verified in Table V. In contrast, even small amounts of pentamethylbenzene interfere.

TABLE V.—INTERFERENCES: $4 \times 10^{-3}M$ TCNE, $0{\cdot}25M$ NAPHTHALENE, $2{\cdot}9 \times 10^{-3}M$ ANTHRACENE (IN 1 hr), PROCEDURE (*b*)

Interference	*M*	% Transmittance
None	—	36·5%
Benzene	0·46	38·0
Toluene	0·188	35·5
Indene	50×10^{-3}	30·5
Phenanthrene	30×10^{-3}	31·5
Chrysene	30×10^{-3}	34·5
Fluoranthene	10×10^{-3}	32·0
Pyridine	6×10^{-3}	66·0
β-Naphthol	30×10^{-3}	31·5
α-Naphthol	10×10^{-3}	41·5
Anthraquinone	0·01 No interference if used as blank	
Cyclopentadiene	0·016	35·0 (Maleic anhydride added)

The interference of a number of polynuclear aromatic hydrocarbons at the $0{\cdot}01M$ level is minimal, with fluoranthene being an exception. Indene, which apparently reacts somewhat with TCNE at the macro level, does not interfere in 1 hr at this level to any greater degree than phenanthrene.

Phenols and aromatic hydrocarbons with an activated position, such as phenanthrene, are C-alkylated by TCNE at room temperature.[15] However, low yields are obtained with phenols unless a catalyst such as pyridine is used.[15] Complexing TCNE with naphthalene apparently slows alkylation of β-naphthol as well as phenanthrene since they do not interfere seriously, as shown in Table V.

Diels-Alder active dienes will interfere since they will react as anthracene. The interference of highly reactive dienes, such as cyclopentadiene, can be minimised by first adding sufficient maleic anhydride to react with the cyclopentadiene, as shown in Table V. Maleic anhydride reacts only very slowly with anthracene at room temperatures.[10] Ammonia, hydrazine, and primary and secondary amines react rapidly with TCNE, releasing hydrogen cyanide. Even a small amount of aniline destroys the red colour of a naphthalene–TCNE complex. Small amounts of pyridine interfere seriously, as shown in Table V.

Alcohols apparently do not react with TCNE without a catalyst such as urea or zinc acetate. Water hydrolyses TCNE slowly, and thiols reduce it.[8]

The effect of heating TCNE-aromatic complexes has been reported to destroy the colour.[16]

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Zusammenfassung—Mengen von bloss 0·5% Anthrazen können in Naphthalin indirekt bestimmt werden. Man misst das Ausbleichen der Farbe des Naphthalin-Tetracyanoathylen (TCÄ)-Komplexes, nachdem Anthracen und TCÄ eine Diels-Alder Reaktion eingegangen sind. Eine Methode für Spurenanalyse basiert auf einer indirekten photometrischen Bestimmung nach diesem Verfahren und dehnt den Mengenbereich herunter zu 0·01% Anthracen in Naphthalin. Pentamethylbenzol kann an Stelle von Naphthalin verwendet werden, aber ist ein weniger gutes Reagens. Eine Anzahl möglicher Störungen wurde studiert.

Résumé—Une quantité aussi faible que 0,5 pour cent d'anthrécène dans le naphtalène peut être dosée indirectement par la mesure de la destruction de la couleur d'un complexe naphtalène-tétracyanoéthylène (TCNE), l'anthracène et le TCNE réagissant au moyen de la réaction de Diels-Alder. Une méthode spectrophotométrique indirecte d'analyse de trace peut être utilisée pour étendre le dosage jusqu'à une quantité aussi faible que 0,01 pour cent d'anthrécène dans le naphtalène. Le pentaméthylbenzène peut être autilisé à la place du naphtalène, mais c'est un réactif moins désirable. Un certain nombre d'interférences possibles ont été étudiées.

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THE FLAME PHOTOMETRIC DETERMINATION OF TRACES OF SODIUM AND POTASSIUM IN THE PRESENCE OF OTHER METALS, AND METHODS FOR OVERCOMING SOME INTERFERENCES

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Summary—A study has been made of the interferences caused by the major metals in the flame photometric determination of sodium and potassium in inorganic salts using an EEL flame photometer. Many metals do not interfere, enabling a straightforward determination to be made. Methods of overcoming the interference of certain other metals include suppression of their flame emissions with aluminium nitrate or their removal by ion-exchange methods before the determination of sodium and potassium.

INTRODUCTION

FLAME photometry provides the simplest method for the determination of small amounts of sodium and potassium, and the Evans Electroselenium Ltd. (EEL) flame photometer[1] is one of the instruments widely employed for this purpose. However, when this instrument is used for the determination of alkali impurities in inorganic salts, in some cases the major metal itself emits radiation which is not completely absorbed by the filters used.

A comprehensive investigation of interference has been carried out for the Perkin Elmer Model 18 instrument,[2] but work with the EEL instrument has been confined to a study of mutual interferences of the alkali metals,[3,4] calcium[5] and some anions.[1]

It was decided to carry out a survey of a fairly wide range of inorganic salts using an EEL instrument in order to discover those metals which cause interferences, and to provide methods for overcoming the difficulty, wherever possible.

EXPERIMENTAL

Apparatus

A standard EEL (Evans Electroselenium Ltd.) flame photometer was used for this work. This instrument, together with its associated filters, has been described by Collins and Polkinhorne.[1]

The preparation of purified solutions of metals and the examination of flame photometric interferences

Purified solutions of the metals were prepared using chemical separation to remove alkali metals when they were known to be present. The methods used are summarised in the Appendix.

The EEL flame photometer was zeroed at full sensitivity against an appropriate blank solution prepared from quantities of reagents similar to those used to prepare the metal solution. Each metal solution was then examined in the EEL flame photometer, and the galvanometer deflection was noted when the sodium and potassium filters were used in turn. Appreciable galvanometer deflections were obtained in many cases (see Table I). In some cases, the transmitted emission was so great that the solution had to be diluted in order to obtain a galvanometer deflection falling within the scale. In such cases the observed deflection was multiplied by the dilution factor. These results were checked by using a different purification procedure and hence it was assumed that the deflections produced were due to emissions from the major metal and not to traces of alkali metals.

TABLE I.—GALVANOMETER DEFLECTIONS FOR INTERFERING METALS

Metal	Method of purification* (see Appendix)	Galvanometer deflection†	
		Sodium filter	Potassium filter
Ba	(a)	71	1200
	(b)	82	1200
Ca	Known to interfere; not examined		
Ce	—	64	69
Cr	(a)	164	220
	(b)	168	152
Co	(a)	59	72
	(b)	58	67
Cu	(a)	22	2
	(b)	29	2
Fe	(a)	140	184
	(b)	136	87
Mn	(a)	56	46
	(b)	56	48
Ni	(a)	62	96
	(b)	78	106
Sr	Known to interfere; not examined		
U	(a)	38	53
	(b)	32	24
	(c)	46	28

* A concentration of 1 g/100 ml was used.
† Full scale deflection (100 units) was given by 2·3 μg/ml of sodium or 3·1 μg/ml of potassium.

All other metals examined gave no significant deflection, and it should therefore be possible to determine sodium and potassium in solutions of these metals by a direct method. To prove this conclusively the recovery of known additions of sodium and potassium from aqueous solutions of commercial salts of these metals was determined. The results obtained are given in Table II.

Throughout this work the addition method of estimating the results was used.[6] This method is simple and is less likely to be affected by interfering elements than other methods, but it is not strictly accurate for sodium as the galvanometer response/concentration curve for this element is not quite linear. The results obtained, however, are sufficiently accurate for normal routine purposes. The results throughout this paper are reported to the nearest 5 ppm.

Except for tungsten, for which erratic results were observed, satisfactory recoveries of sodium and potassium were obtained, especially when it is considered that the percentage recovery was often calculated with reference to high blank values.

It was concluded that sodium and potassium may be directly determined as impurities in solutions of the following metals: aluminium, beryllium, bismuth, cadmium, lead, magnesium, molybdenum, tin, silver, and zinc. Furthermore, it was established that these metals do not affect the approximate linearity of the galvanometer response/concentration curve for sodium and potassium.

Sodium and potassium cannot be directly determined in the presence of those elements which produce interfering flame emissions unless the blank solution contains an equivalent amount of the pure metal. This procedure would not be very satisfactory since, in most cases, it would not be possible to zero the instrument, and this would result in a considerable loss in the working area of the galvanometer scale.

The suppression of interferences with aluminium nitrate

Aluminium nitrate suppresses the flame emissions of calcium[7–9] and strontium.[7,9,10] This has been used to prevent interference from strontium[11] and calcium[8,12] in the determination of sodium.

TABLE II.—RECOVERIES OF SODIUM AND POTASSIUM BY DIRECT FLAME PHOTOMETRY

Metal	Compound used	Metal concentration, % w/v	Sodium			Potassium		
			Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
Al	Aluminium sulphate	1·0	0	140		0	70	125
			200	340	100	200	320	
Be	Beryllium sulphate	0·05	0	10		0	0	80
			200	240	115	200	160	
Bi	Bismuth nitrate	1·0	0	30		0	10	90
			200	250	110	200	190	
Cd	Cadmium chloride	1·0	0	40		0	10	105
			200	260	110	200	220	
Pb	Lead acetate	1·0	0	10		0	0	110
			200	200	95	200	220	
Mg	Magnesium chloride	0·12	0	10		0	20	95
			200	240	115	200	210	
Mo	Ammonium molybdate	0·08	0	130		0	310	100
			200	370	120	200	510	
Sn	Tin^{II} chloride	1·0	0	150		0	10	90
			200	390	120	200	190	
Ag	Silver nitrate	1·0	0	30		0	10	105
			200	240	105	200	220	
W	Ammonium tungstate	1·0	0	60		0	100	30
			200	360	150	200	160	
			0	50		0	180	70
			200	420	185	200	320	
Zn	Zinc sulphate	1·0	0	50		0	10	100
			200	280	115	200	210	

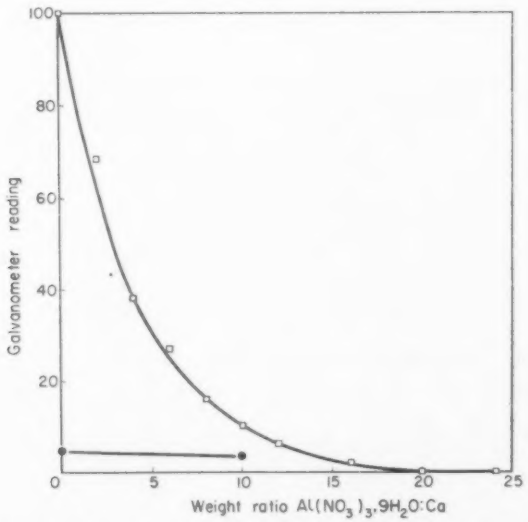

FIG. 1.—The effect of aluminium nitrate on the flame emission of calcium.
□ Na filter
● K filter

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It was decided to investigate the influence of aluminium nitrate on the flame emissions of calcium, strontium, barium and cerium in the determination of sodium and potassium.

Calcium. A series of test solutions was prepared consisting of 1% w/v calcium chloride solution and varying proportions of aluminium nitrate. Each test solution was examined at full sensitivity by the flame photometer, and the scale readings were noted when the sodium and potassium filters were used in turn. The results obtained are given in Fig. 1.

From these results it was concluded that the potassium filter effectively absorbs most of the unwanted emission but that a 20 : 1 weight ratio of aluminium nitrate is required to suppress the calcium emission which passes through the sodium filter.

Known amounts of sodium and potassium were added to a 1% w/v solution of calcium chloride, aluminium nitrate nonahydrate was added in the ratio of 25 : 1 with respect to calcium, and the sodium and potassium were determined flame photometrically, employing the addition technique. The results obtained are given in Table III and show that satisfactory recoveries are possible.

Strontium. Jones[11] has shown that aluminium nitrate may be used to suppress the strontium emission in the determination of sodium.

Tests showed that the strontium emission passing through the potassium filter can be effectively suppressed by adding aluminium nitrate nonahydrate in the weight ratio of 25 : 1 with respect to strontium.

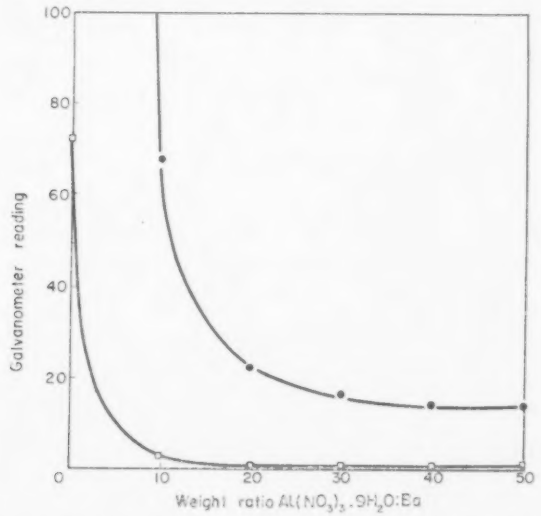

FIG. 2.—The effect of aluminium nitrate on the flame emission of barium.
□ Na filter
● K filter

TABLE III.—DETERMINATION OF KNOWN CONCENTRATIONS OF SODIUM AND POTASSIUM IN CALCIUM CHLORIDE, WITH ALUMINIUM NITRATE NONAHYDRATE PRESENT IN THE WEIGHT RATIO OF 25 : 1 WITH RESPECT TO CALCIUM

Sodium			Potassium		
Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
0	10	—	0	15	—
50	60	100	100	120	105
100	110	100	200	220	105
150	160	100	300	330	105

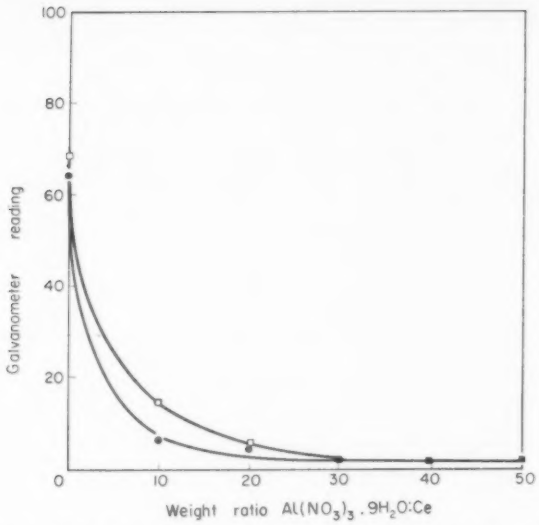

FIG. 3.—The effect of aluminium nitrate on the flame emission of cerium.
□ Na filter
● K filter

Barium and Cerium. Purified 1% aqueous solutions of barium and cerium were prepared as in the Appendix, method (*a*) being used for barium.

Varying proportions of aluminium nitrate were added to the barium and cerium solutions, and these were run through the flame photometer at full sensitivity, after the instrument had been zeroed in each case against a blank solution containing a similar concentration of aluminium nitrate. The galvanometer deflections obtained are given in Figs. 2 and 3.

The results showed that the flame emission of cerium which normally passes through the sodium and potassium filters may be almost completely suppressed by a thirty-fold weight of aluminium nitrate nonahydrate.

A similar proportion of aluminium nitrate also successfully suppressed the barium flame emission passing through the sodium filter. The results obtained for barium and the potassium filter were inconclusive and a further check was made, using 1% barium solutions prepared directly from AnalaR barium chloride, and from barium chloride followed by single and double precipitations with ammonium carbonate.

Employing a 45% concentration of aluminium nitrate and the potassium filter a galvanometer deflection of about 16 units was obtained in each case. It was concluded that it is not possible to suppress completely that part of the barium flame emission which passes through the potassium filter.

The recovery of known additions of sodium and potassium from ammonium cerium^{IV} nitrate

Using a 1% w/v solution of ammonium cerium^{IV} nitrate to which known additions of sodium and potassium had been made, it was found possible to obtain good recoveries after the addition of 10% w/v hydrated aluminium nitrate. The results are shown in Table IV.

The effect of aluminium nitrate on the flame emissions of certain other metals

Aluminium nitrate was found to be ineffective in the suppression of unwanted radiation in the case of the following metals: chromium, manganese, iron, uranium, nickel, cobalt, and copper.

The removal of some interfering metal ions by ion-exchange methods

Ion-exchange techniques are now widely used for removing interfering ions in various analytical methods and it seemed likely that some of these techniques could be used for the removal of interfering ions before the flame photometric determination of sodium and potassium.

Copper was not investigated as it can be readily removed by electrolysis.

TABLE IV.—RECOVERY OF SODIUM AND POTASSIUM FROM AMMONIUM CERIUM^{IV} NITRATE

Sodium			Potassium		
Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
0	140	—	0	15	—
0	150	—	0	5	—
0	150	—	0	5	—
50	210	120	50	65	110
100	265	115	100	120	110

Chromium^{VI} and Manganese^{VII}. Preliminary tests showed that 0·5 g of chromium, as potassium dichromate, was readily absorbed on a 1- × 20-cm column of Amberlite IRA-400(Cl) resin.

On this basis, the following procedure was tried:

A 1- × 20-cm column of Amberlite IRA-400(Cl) was prepared and washed well with water. The sample solution, containing 0·5 g of the chromium^{VI} and known additions of sodium and potassium dissolved in about 10 ml of water, was allowed to pass down the column at the rate of about 1 drop/sec. One hundred ml of water were then passed down the column at about 2 drops/sec. The combined eluate was reduced to a volume of 50 ml by evaporation and dilution to volume in a graduated flask, and sodium and potassium were determined in the usual way.

A similar procedure was used for manganese^{VII} in the form of potassium permanganate, with the exception that the sample was dissolved in 25 ml of water, instead of in 10 ml, and the solution was passed through the column at a rate of 2 drops/sec.

The recoveries of sodium and potassium obtained are shown in Table V. The apparent sodium and potassium contents found without separation are also listed.

TABLE V.—RECOVERIES OF SODIUM AND POTASSIUM FROM POTASSIUM PERMANGANATE, POTASSIUM DICHROMATE AND CHROMIUM TRIOXIDE, USING AN IRA-400 (Cl) COLUMN FOR REMOVAL OF THE INTERFERING ION

Compound	Proposed Method						Without Separation	
	Sodium			Potassium			Sodium	Potassium
	Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %	Found, *ppm*	Found, *ppm*
Potassium permanganate (4 samples)	0	95	—	—	—	—	210	—
	200	300	105					
	0	75	—					
	200	290	110					
	0	120	—					
	200	320	100					
	0	100	—					
	200	320	110					
Potassium dichromate	0	510	—	—	—	—	1100	—
	200	700	95					
Chromium trioxide (2 samples)	0	205	—	0	40	—	615	550
	200	435	115	200	240	100		
	0	220	—	0	30	—		
	200	460	120	200	210	90		

The results showed that this technique effectively removed manganese^{VII}, and chromium^{VI} and good recoveries of sodium and potassium were obtained.

Uranium. In sulphuric acid solution, uranium forms a complex anion, $[UO_2(SO_4)_n]^{2-2n}$, which may be absorbed by quaternary anion-exchange resins and this fact has been widely used as a technique for separating uranium from other elements.[14–18]

A column of Amberlite IRA-400 in the sulphate form was prepared and it was found that absorption of the uranium was complete from solutions 0·1*N* with respect to sulphuric acid.

The sample, containing about 0·5 g of uranium and known additions of sodium and potassium, was dissolved in 10 ml of 0·1*N* sulphuric acid and the solution was passed down a 1 × 30-cm column of Amberlite IRA-400(SO_4). The column was allowed to run at a rate of 1 drop/sec. The column was washed with 100 ml of 0·1*N* sulphuric acid, and the combined eluate was reduced to a volume of 50 ml by evaporation and adjustment in a graduated flask. The sodium and potassium were then determined in the usual way. The compounds used were AnalaR uranyl nitrate and AnalaR uranyl acetate, and the results obtained are given in Table VI.

TABLE VI.—RECOVERIES OF SODIUM AND POTASSIUM FROM URANIUM SALTS, USING AN IRA-400(SO_4) COLUMN FOR REMOVAL OF THE URANIUM

Compound	Sodium			Potassium		
	Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
Uranyl nitrate	0	80	—	0	25	—
	200	280	100	200	210	95
Uranyl acetate	0	100	—	0	20	—
	200	305	105	200	230	105

The results showed that the uranium had been effectively removed from the solution, and good recoveries of sodium and potassium were obtained.

Manganese^{II}, *Nickel*, *Cobalt*, *Chromium*^{III} *and Iron.* Samuelson *et al.*[19,20] have developed a method for separating alkali metals from many other metals when both constituents are present in approximately equal amounts. They passed the solution down a column of a strong anion-exchange resin (Dowex 2) in the EDTA-form. The interfering metal was held by the resin as its EDTA complex while the alkali metals passed through in the eluate.

It was decided to apply this technique to the separation of traces of alkali metal impurities from the interfering metals.

Amberlite IRA-400(Cl) was used, this being an equivalent of Dowex 2. Samuelson *et al.*[19] converted the resin to the EDTA form by successive treatments with sodium acetate and disodium ethylenediaminetetra-acetate. For this work, ammonium salts were used to avoid contaminating the resin with sodium.

The resin column was prepared as follows:

A slurry of Amberlite IRA-400(Cl) was tipped into a 1-cm diameter glass column to a height of about 60 cm. Two hundred ml of 10% w/v ammonium acetate solution was passed through the column at a rate of 1 drop/sec. The column was then washed with 100 ml of water.

Ten g of ethylenediaminetetra-acetic acid was suspended in 100 ml of water and ammonium hydroxide solution (sp. gr. 0·880) was added until the free acid had dissolved. The filtered solution was allowed to percolate through the column at a rate of 1 drop/sec. Finally the column was washed with 500 ml of water.

This procedure was also found to be suitable for the regeneration of a column loaded with nickel, cobalt or manganese. Chromium was tenaciously held by the column and 600 ml of 10% w/v ammonium acetate solution was necessary to remove it. Iron^{III} was best removed by ammonium acetate solution which had been half-saturated with sulphur dioxide.

Procedure. The sample containing about 0·25 g of the interfering element, was dissolved in 10 ml of water and the solution was transferred to the column, which was allowed to run at a rate of

1 drop/sec. The column was washed with 100 ml of water, and the combined eluate was adjusted to 25 ml by evaporation and dilution in a graduated flask. The sodium and potassium were determined by the addition technique in the usual way.

Analyses were carried out on samples to which known quantities of sodium and potassium had been added. The recoveries obtained are given in Table VII.

The results were satisfactory, considering the large blank values which had to be taken into account. Erratic results were obtained for iron^{III} salts. In several cases, considerable quantities of iron passed into the eluate. Incomplete absorption was also obtained with chromium.

TABLE VII.—THE RECOVERY OF SODIUM AND POTASSIUM FROM SALTS OF NICKEL, MANGANESE^{II} AND COBALT BY THE PROPOSED METHOD

Compound	Sodium			Potassium		
	Added, *ppm*	Found, *ppm*	Recovery, %	Added, *ppm*	Found, *ppm*	Recovery, %
Nickel chloride	0	95	—	0	20	—
	200	290	95	200	180	80
Manganese^{II} sulphate	0	295	—	0	120	—
	800	1025	90	200	280	80
Manganese^{II} acetate	0	205	—	0	370	—
	200	435	115	200	560	95
Cobalt chloride	0	410	—	0	30	—
	200	630	110	200	180	75
Cobalt nitrate	0	2700	—	0	430	—
	200	2900	100	200	570	70

ANALYTICAL PROCEDURES FOR THE DETERMINATION OF TRACES OF SODIUM AND POTASSIUM IN THE PRESENCE OF OTHER METALS

(*a*) *Simple method in the presence of aluminium, beryllium, bismuth, cadmium, lead, magnesium, molybdenum, tin, silver, and zinc*

Reagents

Standard sodium and potassium solutions [see (*b*)].

Procedure

Dissolve a suitable quantity (usually 0·5–1·0 g) of the sample in water or the minimum amount of dilute acid and dilute to 100 ml. To 50 ml of the solution, add 0·5 ml of standard sodium solution (1 ml ≡ 100 μg of Na) and 0·5 ml of standard potassium solution (1 ml ≡ 200 μg of K). Retain the remaining 50 ml of solution. Run each half of the solution through the EEL flame photometer in turn, employing the appropriate filter, and note the galvanometer deflections. If the galvanometer deflection is off the scale repeat the determination with a smaller quantity of the sample.

Calculate the sodium and potassium contents in the following way:

$$\text{Concentration of sodium/potassium (ppm)} = \frac{ad}{(b-a)c}$$

where a = galvanometer deflection due to sample,
b = galvanometer deflection due to sample and standard,
c = concentration of sample (g/100 ml),
and d = concentration of standard (μg/ml).

(*b*) *Method in the presence of calcium, strontium and cerium*

Reagents

Aluminium nitrate solution: Dissolve 50 g of aluminium nitrate, $Al(NO_3)_3.9H_2O$, in water and dilute to 100 ml with water. Filter if necessary.

Standard sodium solution: Dissolve 0·254 g of dry sodium chloride in water and dilute to 1 litre (1 ml ≡ 100 μg of Na).

Standard potassium solution: Dissolve 0·382 g of dry potassium chloride in water and dilute to 1 litre (1 ml ≡ 200 μg of K).

Procedure

Dissolve a suitable quantity (usually 0·5–1·0 g) of the sample in water or in the minimum amount of 5*N* hydrochloric acid.

For calcium and strontium: Add aluminium nitrate solution in the ratio of 5 ml for every 0·1 g of calcium or strontium present.

For cerium: Add aluminium nitrate solution in the ratio of 6 ml for every 0·1 g of cerium present.

Prepare a blank solution containing the same quantity of aluminium nitrate and dilute the sample and blank solution to 100 ml. Continue as in (*a*), zeroing the flame photometer against the blank solution.

(*c*) *Method in the presence of manganese, nickel and cobalt*

Reagents

Ammonium acetate solution: Dissolve 20 g of ammonium acetate in 200 ml of water.

EDTA di-ammonium salt: Suspend 10 g of ethylenediaminetetra-acetic acid in 100 ml of water. Stir continuously and add ammonium hydroxide (sp. gr. 0·880) until a clear solution is obtained. Filter before use.

Amberlite IRA-400(*Cl*) *resin, analytical grade.*

Standard sodium solution: as in (*b*).

Standard potassium solution: as in (*b*).

Preparation and regeneration of the resin: Make a slurry of the resin and pour this into a 1-cm diameter glass column to a height of about 60 cm. Treat the column successively with the following solutions: 200 ml of 10% w/v ammonium acetate at 1 drop/sec, 100 ml of water at a fast rate, 100 ml of 10% w/v EDTA di-ammonium salt at 1 drop/sec, and 500 ml of water at a fast rate.

Procedure

Dissolve the sample, containing not more than 0·25 g of the interfering metal, in 10 ml of water. If the compound is not water-soluble, dissolve in dilute hydrochloric acid, evaporate to low volume and dilute to 10 ml with water. Transfer the solution to the column and run the column at a rate of about 1 drop/sec. Wash the column with 100 ml of water. Evaporate the eluate and dilute to 100 ml in a graduated flask. Continue as in (*a*).

(*d*) *Method in the presence of manganese*^{VII} *and chromium*^{VI}

Procedure

Prepare a 1- × 20-cm column of Amberlite IRA-400(Cl). Wash with water until the eluate is free of sodium and potassium. Dissolve the sample containing not more than 0·5 g of chromium^{VI} or manganese^{VII} in the minimum quantity of water, and transfer the solution to the column.

Run the column at about 1 drop/sec for chromium^{VI} and 2 drops/sec for manganese^{VII}, adding sufficient water to keep the column wet. Wash with 100 ml of water at 2 drops/sec for chromium^{VI} and 4 drops/sec for manganese^{VII}. Reject the used resin. Adjust the eluate to 100 ml by evaporation and dilution in a graduated flask. Continue as in (*a*).

(*e*) *Method in the presence of uranium*

Reagents

5*N sulphuric acid:* Dilute 136 ml of sulphuric acid to 1 litre.

0·1*N sulphuric acid:* Dilute 20 ml of 5*N* sulphuric acid to 1 litre.

5*N ammonium carbonate:* Dissolve 200 g of ammonium carbonate in a mixture of water and 250 ml of 5*N* ammonium hydroxide. Dilute to 1 litre.

Amberlite IRA-400(*Cl*)*:* Use the analytical-grade resin.

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Standard sodium solution: as in (*b*).

Standard potassium solution: as in (*b*).

Preparation and regeneration of the resin: Prepare a slurry of Amberlite IRA-400(Cl) and pour this into a glass column of internal diameter 1 cm until a height of about 30 cm is reached. Convert the resin to the sulphate form by running 100 ml of 5*N* sulphuric acid through it at about 1 drop/sec. Wash the column with water until the eluate is free of chloride.

The resin should be regenerated immediately after use as uranium is slowly reduced on the resin. Place the resin in a beaker and stir with 50-ml portions of 5*N* ammonium carbonate until the supernatant liquid is no longer coloured. Stir with two 50-ml portions of 5*N* sulphuric acid. Return the resin to the column and wash thoroughly with water.

Procedure

Dissolve the sample, containing not more than 0·5 g of uranium, in 10 ml of 0·1*N* sulphuric acid, and transfer the solution to the column. Run the column at about 1 drop/sec and wash with 100 ml of 0·1*N* sulphuric acid. Adjust the volume of the eluate to 100 ml by evaporation and dilution in a graduated flask. Continue as in (*a*).

Metal	*Procedure*	*Approximate concentration*
Aluminium	Aluminium wire dissolved in 2 : 1 hydrochloric acid: nitric acid.	0·5% Al
Barium	(*a*) Barium acetate dissolved in water; barium precipitated with ammonium carbonate; barium carbonate filtered, dissolved in 5*N* hydrochloric acid. (*b*) Barium carbonate washed with hot water; dissolved in 5*N* hydrochloric acid.	1% Ba
Beryllium	Beryllium sulphate dissolved in water; ammonium carbonate added; beryllium carbonate filtered, dissolved in 5*N* hydrochloric acid.	0·05% Be
Bismuth	Bismuth ingot dissolved in 5*N* nitric acid.	1% Bi
Cadmium	Cadmium chloride dissolved in water, cadmium precipitated with hydrogen sulphide; cadmium sulphide filtered and dissolved in 2 : 1 hydrochloric acid : nitric acid.	1% Cd
Calcium	Known to interfere; not examined.	—
Cerium	Ammonium cerium^{IV} nitrate dissolved in water, and cerium precipitated with ammonium hydroxide; cerium^{IV} hydroxide filtered, dissolved in 5*N* hydrochloric acid.	1% Ce
Chromium	(*a*) Ammonium dichromate dissolved in water; passed through Amberlite IRA-400(Cl) column; column washed with water and chromium eluted with 5*N* hydrochloric acid, saturated with sulphur dioxide. (*b*) Chromium^{III} chloride dissolved in water and chromium precipitated with excess ammonium hydroxide; chromium^{III} hydroxide dissolved in 5*N* hydrochloric acid.	1% Cr

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Metal	*Procedure*	*Approximate concentration*
Cobalt	(*a*) Cobalt chloride dissolved in water; cobalt precipitated with hydrogen sulphide; cobalt sulphide filtered, dissolved in 2 : 1 hydrochloric acid:nitric acid. (*b*) Cobalt chloride dissolved in 9*M* hydrochloric acid and passed down Amberlite IRA-400(Cl) column. Column washed with 9*M* hydrochloric acid and cobalt eluted with water.[21,22]	1% Co
Copper	(*a*) Copper foil dissolved in 5*N* nitric acid. (*b*) Copper sulphate dissolved in dilute sulphuric acid; solution electrolysed using platinum electrodes; deposited copper dissolved from cathode with 5*N* nitric acid.	1% Cu
Iron	(*a*) Electrolytic iron dissolved in 5*N* hydrochloric acid. (*b*) Iron^{III} chloride dissolved in hydrochloric acid; iron extracted with 2,2′-dichlorodiethyl ether; ether layer washed with hydrochloric acid; iron extracted with 0·5*N* hydrochloric acid.[23]	1% Fe
Lead	Lead foil dissolved in 5*N* nitric acid.	1% Pb
Magnesium	Magnesium ribbon dissolved in 5*N* hydrochloric acid.	0·5% Mg
Manganese	(*a*) Manganese^{II} sulphate dissolved in water; excess thioacetamide added; solution boiled; manganese^{II} sulphide filtered and dissolved in 5*N* hydrochloric acid. (*b*) Electrolytic manganese dissolved in 5*N* hydrochloric acid.	1% Mn
Molybdenum	Ammonium molybdate dissolved in water; solution passed through Amberlite IRA-400(Cl) column; molybdenum eluted with 5*N* ammonium hydroxide; excess evaporated.	0·5% Mo
Nickel	(*a*) Nickel chloride dissolved in water; nickel precipitated with hydrogen sulphide; nickel sulphide filtered and dissolved in 2 : 1 hydrochloric acid:nitric acid. (*b*) Nickel wire dissolved in 2 : 1 hydrochloric acid: nitric acid.	1% Ni
Silver	Silver nitrate dissolved in water; silver precipitated with 5*N* hydrochloric acid; silver chloride filtered and dissolved in 5*N* ammonium hydroxide. Excess *not* evaporated.	1% Ag
Tin	Tin^{II} chloride dissolved in water acidified with hydrochloric acid; tin precipitated with hydrogen sulphide; tin^{II} sulphide filtered and dissolved in hydrochloric acid.	1% Sn

Metal	*Procedure*	*Approximate concentration*
Tungsten	Ammonium tungstate dissolved in water; excess 5*N* hydrochloric acid added and solution boiled; tungstic acid filtered and dissolved in 5*N* ammonium hydroxide; excess *not* evaporated.	1% W
Uranium	(*a*) Uranyl nitrate dissolved in 1 : 10 nitric acid containing 70% ammonium nitrate; uranium extracted with diethyl ether,[24] ether layer washed with water and evaporated almost to dryness. (*b*) Uranyl acetate dissolved in water, uranium precipitated with ammonium hydroxide; ammonium di-uranate filtered and dissolved in 5*N* hydrochloric acid. (*c*) Uranyl acetate dissolved in water; uranium extracted with acetyl acetone-carbon tetrachloride mixture at pH 7;[25] uranium extracted with 50 ml of water containing 10 ml of 5*N* hydrochloric acid.	1% U
Zinc	Zinc dissolved in 5*N* nitric acid.	1% Zn

APPENDIX

Methods used for preparation of alkali-free solutions

AnalaR chemicals were used wherever possible, and in each case the excess acid used during the preparation was removed by evaporation almost to dryness, and the residue was dissolved in water.

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Zusammenfassung—Die durch das Hauptmetall verursachten Störungen in der flammphotometrischen Bestimmung von Natrium und Kalium mit einem "EEL"-Flammphotometer werden untersucht. Zahlreiche Metall stören nicht. Methoden zur Ausschliessung der Störungen verschiedener anderer Metalle werden beschrieben wie z.B. Unterdrückung der Flammemmission durch Zusatz von Aluminiumnitrat oder Abtrennung der Störmetalle mittels Ionenaustauscher.

Résumé—Les auteurs ont étudié les interférences dues au métal principal dans le dosage des sels de sodium et de potassium par photométrie de flamme, utilisant un photomètre de flamme "EEL". De nombreux métaux ne gênent pas, ce qui permet de faire un dosage direct. Des méthodes pour éliminer l'interférence de certains autres métaux nécessitent la suppression de leurs émissions de flamme par du nitrate d'aluminium, ou leur séparation par des méthodes d'échange d'ions, avant le dosage du sodium et du potassium.

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THE DETERMINATION OF TRACES OF OSMIUM AND IRIDIUM IN SAMPLES OF PALLADIUM AND PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A method is described for the determination of ultramicro quantities of osmium and iridium in samples of palladium and platinum. In order to avoid self-shielding differences between samples and standards during neutron irradiation, standards have been prepared by the addition of very small known amounts of osmium and iridium to analytical samples. In the analysis of palladium samples the Harwell Pile BEPO has been used as the neutron source. To avoid spurious results due (n,p) and (n,α) reactions, the Pile DIDO has had to be used for neutron-activation of samples of platinum. Each determination requires 0·1 g of sample, and radiochemical separations using carriers have been used to isolate the induced osmium and iridium activities. Results are quoted for the osmium and iridium contents of some pure palladium and platinum samples.

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INTRODUCTION

ONE of the most complex problems in experimental inorganic chemistry is the separation of platinum metals in a high state of purity. This is of considerable importance as the electrical and mechanical properties of the metals are markedly affected by minute quantities of impurities. Hitherto, spectrographic and spectrophotometric methods of analysis have been most extensively employed to determine such trace constituents, but in many cases these procedures do not provide sufficient sensitivity.

Neutron-activation analysis permits the determination of many elements in ultramicro quantities, and the application of this method to the determination of traces of osmium and iridium in samples of palladium and platinum is reported here.

Neutron-activation procedures have been used previously for the determination of osmium and iridium in various materials. Smales[1] has reported the determination of iridium in a sample of rhodium. The decay curve of the irradiated rhodium showed two components, 74-day iridium-192 and 19·0-hour iridium-194, and no radiochemical separation was necessary.

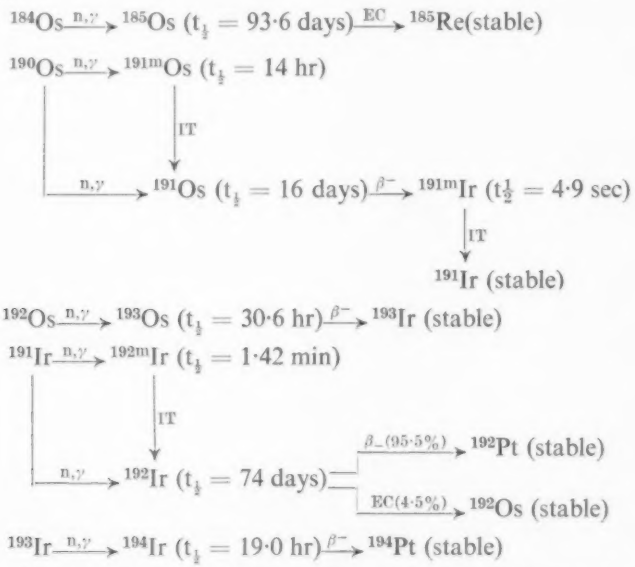
Zvyagintsev and Kulak[2] have investigated the determination of iridium and other precious metals in refined silver by activation analysis, and Italian workers[3] have reported semiquantitative methods for iridium in platinum.

Miller[4] has studied the neutron-activation analysis of elements of Group VIII of the periodic table, and he gives considerable information on nuclear reactions of osmium and iridium and the assay of resulting radionuclides. It has been indicated[5] that at the Oak Ridge National Laboratory neutron-activation has been applied to the determination of osmium in iron and palladium and to the determination of iridium in rhodium chloride and palladium. Analyses showed 10–100 ppm of osmium and 4–5 ppm of iridium in samples of palladium.

Neutron-activation has been used in isotope abundance analysis of osmium.[6]

NEUTRON-ACTIVATION OF OSMIUM AND IRIDIUM

Naturally occurring osmium consists of seven isotopes, ^{184}Os (per cent abundance $\theta = 0{\cdot}018$), ^{186}Os ($\theta = 1{\cdot}59\%$), ^{187}Os ($\theta = 1{\cdot}64\%$), ^{188}Os ($\theta = 13{\cdot}3\%$), ^{189}Os ($\theta = 16{\cdot}1\%$), ^{190}Os ($\theta = 26{\cdot}4\%$) and ^{192}Os ($\theta = 41{\cdot}0\%$). Iridium exists as two stable isotopes, ^{191}Ir ($\theta = 38{\cdot}5\%$) and ^{193}Ir ($\theta = 61{\cdot}5\%$). On irradiation with neutrons of thermal energies, osmium and iridium give rise to radionuclides by the following nuclear reactions:


184Os n,γ 185Os (t½ = 93·6 days) EC 185Re(stable)
190Os n,γ 191mOs (t½ = 14 hr)
IT
n,γ 191Os (t½ = 16 days) β− 191mIr (t½ = 4·9 sec)
IT
191Ir (stable)
192Os n,γ 193Os (t½ = 30·6 hr) β− 193Ir (stable)
191Ir n,γ 192mIr (t½ = 1·42 min)
IT
n,γ 192Ir (t½ = 74 days)
β− (95·5%) 192Pt (stable)
EC(4·5%) 192Os (stable)
193Ir n,γ 194Ir (t½ = 19·0 hr) β− 194Pt (stable)

Relevant isotopic thermal neutron-activation cross-sections, σ, in barns, are:[7]

^{184}Os	$\sigma < 200$
^{190}Os	$\sigma = 8$ (16 days)
^{192}Os	$\sigma = 1{\cdot}6$
^{191}Ir	$\sigma = 260$ (1·4 min)
	$\sigma = 700$ (74 days)
^{193}Ir	$\sigma = 130$.

A summary of nuclear data for the different radionuclides produced in the nuclear reactions[8] is given in Table I.

It has been estimated[9] that with a thermal neutron flux of 10^{12} neutrons/cm^2/sec, it should be possible under ideal conditions to determine 1×10^{-9} g of osmium utilising 30·6-hr ^{193}Os with 16-day ^{191}Os. The corresponding calculated sensitivity for iridium is 1×10^{-11} g, using 19-hr ^{194}Ir with 74-day ^{192}Ir.

In the present study a comparative procedure involving simultaneous irradiation of samples and standards has been employed. The thermal neutron absorption cross-sections[7] for osmium, iridium, platinum and palladium are considerable, *viz:*

Os	$\sigma = 15{\cdot}3$ barns
Ir	$\sigma = 440$
Pt	$\sigma = 8{\cdot}8$
Pd	$\sigma = 8{\cdot}0$.

TABLE I.—NUCLEAR DATA FOR RADIONUCLIDES PRODUCED FROM OSMIUM AND IRIDIUM BY (n,γ) REACTIONS.

Radionuclide	Half-life	Radiations and energies, *MeV*
^{185}Os	93·6 days	EC; γ 0·07 to 0·88
^{191m}Os	14 hr	IT e$^-$ (γ) 0·074
^{191}Os	16·0 days	β^- 0·143; γ e$^-$ (with ^{191m}Ir) 0·042, 0·129
^{193}Os	30·6 hr	β^- 1·14 (40%), 1·06 (33%), 1·00 (5%) 0·86 (12%), 0·68 (10%); γ 0·073 to 0·460
^{192m}Ir	1·42 min	IT e$^-$ (γ) 0·058 (99·9%); β^- (c.0·1%)
^{192}Ir	74·37 days	β^- 0·67, others (95·5%); EC (4·5%); γ 0·316 0·296, 0·308. 0·468 (others)
^{194}Ir	19·0 hr	β^- 2·24 (66%), 1·91 (15%), 0·98 (10%), 0·43 (*ca.*8%); γ 0·33, (others 0·29 to 2·05)

To avoid neutron self-shielding differences between samples and standards, therefore, standards have been prepared by the admixture of very small known quantities of osmium and iridium with analytical samples.

EXPERIMENTAL

Irradiation

Samples of palladium or platinum powder, *ca.* 0·1 g, were accurately weighed and sealed in silica irradiation tubes of 6-mm internal diameter. Standards were prepared by the addition of weighed portions (*ca.* 0·05 g) of standard solutions of osmium (80 mg of Os/litre, as $(NH_4)_2OsCl_6$ in 3*M* HCl) and iridium (20 mg of Ir/litre, as $(NH_4)_2IrCl_6$ in 3*M* HCl) to 0·1-g samples of platinum and palladium in silica irradiation tubes. The liquid was allowed to soak into the metal powder, then carefully evaporated to dryness, after which the tubes were sealed.

Samples, together with standards containing added osmium and iridium, were packed with silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron-irradiation. In the case of samples of palladium, irradiation was for 1 week in the Pile BEPO with a thermal neutron flux of 10^{12} neutrons/cm^2/sec. Samples of platinum were irradiated for 1 week in a thermal neutron flux of 9×10^{11} neutrons/cm^2/sec in the Pile DIDO (see Discussion).

Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were put through a radiochemical procedure to obtain the necessary separation of osmium and iridium radionuclides. Carrier chemistry was used in the procedure.

Osmium was separated by distillation of the tetroxide, OsO_4. Further purification was obtained by precipitation of hydrous OsO_2, which was subsequently reduced to metal, in which form the osmium was counted.

Following the removal of osmium by distillation, iridium was separated from palladium or platinum by precipitation of the latter elements with calomel in the presence of bromide.[10] Further purification of the iridium was obtained by precipitation of hydrous IrO_2 using $NaBrO_3$ and $NaHCO_3$. After dissolving the precipitate in HCl and fuming with $HClO_4$, the iridium was extracted into pyridine[11] and subsequently was precipitated again as the hydrous dioxide. The dioxide was finally reduced to metal, in which form the iridium was counted.

Preparation and standardisation of carriers

Osmium: Dissolve a weighed quantity of pure recrystallised $(NH_4)_2OsCl_6$ in 3*M* HCl to give a solution containing 5 mg of Os/ml.

Pipette 5 ml of the carrier solution into a weighed porcelain crucible placed inside a large Vitreosil Rose crucible. Pass a stream of hydrogen through the Rose crucible cover, and heat gently. When the solution has evaporated, heat strongly for 30 min, continuing the passage of hydrogen. Cool in

hydrogen and weigh the residue as Os. (If there are any black particles in the Rose crucible after the ignition these should be transferred to the inner crucible and included with the residue.)

Iridium: Dissolve 2·3 g of pure $(NH_4)_2IrCl_6$ in 6*M* HCl and dilute to 1 litre with 2% HCl.

Pipette 10 ml of the carrier into a 250-ml beaker and evaporate carefully until the volume is reduced to *ca.* 2 ml. Add 15 ml of 16*M* HNO_3 and 5 ml of 70% $HClO_4$ and evaporate until fumes of $HClO_4$ begin to be evolved. Cool and add 20 ml of warm water. Filter through a small paper to remove silica or other insoluble matter and wash the paper well with 5% $HClO_4$. Collect the filtrate and washings in a 250-ml beaker. Dilute to 100 ml and boil for *ca.* 10 min with 10 ml of 5% $Hg(NO_3)_2$ solution and 5 drops of 10% $NaBrO_3$. Digest for a further 10 min on a water-bath. Decant the solution through a Whatman No. 41 paper, rinse the precipitate on to the paper, and wash well with hot water. Place the paper in a weighed porcelain crucible, dry it and impregnate it with a few drops of saturated NH_4Cl solution. Char the paper at a low temperature and heat the residue at 900° for 10 min. Reduce in hydrogen. Brush the metal powder quantitatively into a platinum crucible and treat with 40% HF, then with 6*M* HNO_3. Evaporate to dryness. Transfer the iridium quantitatively to the original porcelain crucible, reduce and cool in hydrogen and weigh as Ir.

Radiochemical separation procedure

Treat each sample and standard in the following manner:

Step 1. Remove a silica irradiation tube from the can, open it at the constriction and transfer the contents quantitatively to a 250-ml Quickfit distillation flask. Wash out the tube thoroughly with hot 6*M* HCl and transfer the washings to the flask. Add 10 ml of standard Ir-carrier, 4 ml of standard Os-carrier, 5 ml of 12*M* HCl and 5 ml of 18*M* H_2SO_4.

Step 2. Connect the distillation flask, fitted with a dropping funnel, to form an osmium distillation apparatus; join the flask to a train of three receivers, the first containing 1% $KMnO_4$, the second and third each containing 100 ml of 2*M* NaOH and 5 ml of methyl alcohol [Note (*a*)]. Connections should be made through Quickfit spherical joints to permit a degree of flexibility. Connect the final receiver to a suction pump to enable a stream of air to be drawn through the entire train. Cool the receivers containing alcohol-NaOH by surrounding them with ice.

Step 3. Add 20 ml of 16*M* HNO_3 to the distillation flask and heat gently until the metal sample has dissolved, then heat strongly. After *ca.* 10 min, heat the receiver containing $KMnO_4$ solution and continue heating until no trace of brown fumes can be seen in the flask [Note (*b*)]. Retain the contents of the second receiver for *osmium determination* and the residue in the distillation flask for *iridium determination*.

Step 4. *Determination of Osmium.* Transfer the alkaline solution from the second receiver to a 250-ml beaker and neutralise approximately with 12*M* HCl. Heat to 60° and neutralise more exactly (green colour using Universal indicator paper) with 4*M* H_2SO_4 and Na_2CO_3 solution. Digest on a water-bath for a few min, and allow the black precipitate of hydrous OsO_2 to settle. Decant off and discard the supernate. Wash the precipitate thoroughly with saturated NH_4Cl solution.

Step 5. Transfer the hydrous OsO_2 as a slurry to a porcelain crucible. Warm gently to remove any liquid, then ignite under hydrogen for 15 min. Cool the residue under hydrogen and brush it on to a tared aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068). Make sure that the distribution of osmium powder on the tray is uniform. Weigh to establish the chemical yield.

Step 6. *Determination of Iridium.* Evaporate the residual solution from the osmium distillation to small volume. Cautiously add 12*M* HCl dropwise until all nitrous fumes cease to be evolved [Note (*c*)].

Step 7. Add 50 ml of water and 2·5 g of solid NaBr and boil. Add Hg_2Cl_2 (in the form of a freshly prepared paste in water) in portions until the solution turns yellow-green. Digest for 10 min on a water-bath.

Step 8. Filter through a Whatman No. 41 paper and wash the precipitate with hot 2% HCl. Retain the filtrate and washings in a 250-ml beaker.

Step 9. Dilute the filtrate to 150 ml with water, boil, and add 10 ml of 10% $NaBrO_3$ solution. Neutralise to the end-point of bromocresol purple with 10% Na_2CO_3 solution. Boil for 10–15 min. Add a further 10 ml of 10% $NaBrO_3$ and adjust to pH 8. Allow the flocculent precipitate of hydrous IrO_2 to settle and transfer it by filtration onto a Whatman No. 41 paper.

Step 10. Wash the precipitate into a 250-ml beaker with H_2O and dissolve it by the addition of 12*M* HCl and heating on a hot-plate. Evaporate the solution to small volume. Add 10 ml of 70%

$HClO_4$ and fume for *ca.* 15 min until the solution turns deep violet-blue in colour. Cool the solution.

Step 11. Add 10 ml of water and 20 ml of pyridine. Place in a separating funnel and add 19*M* NaOH to separate the pyridine layer. Wash the dark blue pyridine phase three times with equal volumes of 6*M* HCl, separating the layers each time with 6*M* NaOH.

Step 12. Add a few drops of 6*M* NaOH to the pyridine layer and evaporate off the pyridine.

Step 13.Take up the residue in 12*M* HCl and transfer to a 250-ml beaker. Evaporate the solution to small volume and add 15 ml of 16*M* HNO_3 and 5 ml of 70% $HClO_4$. Boil until slight fumes of $HClO_4$ begin to be evolved [Note(*d*)]. Cool the solution, add 20 ml of water and filter [Note (*e*)]. Wash the filter paper with warm 5% $HClO_4$. Collect the filtrate and washings in a 250-ml beaker and dilute to 150 ml with water. Boil with 10 ml of 5% $Hg(NO_3)_2$ and 5 drops of 10% $NaBrO_3$ for 10 min. Digest for a further 10 min. Filter through a Whatman No. 44 paper, and wash the precipitate of hydrous IrO_2 thoroughly with hot H_2O followed by saturated NH_4Cl solution.

Step 14. Transfer the paper and precipitate to a porcelain crucible. Char the paper slowly, then heat to 900° for 10 min. Reduce and cool the residue under hydrogen and brush it on to a tared aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068). Make sure that the distribution of the iridium powder on the tray is uniform. Weigh to establish the chemical yield.

Notes

(*a*) The distillation should be performed in an efficient fume-cupboard. OsO_4 is extremely toxic and the third receiver is used as a precaution to prevent any possible escape of the compound.

(*b*) RuO_4 is not formed under the experimental conditions and hence does not contaminate the osmium distillate (see also Forsyth and Morris[12]).

(*c*) HNO_3 must be removed at this stage.

(*d*) This is to remove Cl^-.

(*e*) The filtration is to remove SiO_2 or other insoluble impurities.

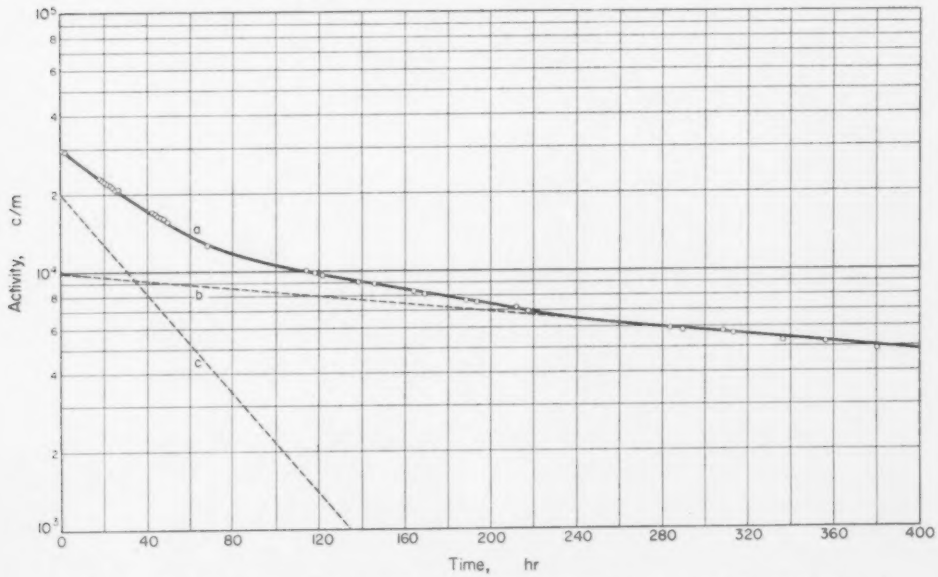


FIG. 1.—Part of a composite decay curve of osmium separated from an analysis standard:
(*a*) Composite decay curve.
(*b*) Osmium-191 activity (observed $t_{\frac{1}{2}} = 16{\cdot}2 \pm 1$ days)
(*c*) Osmium-193 activity (observed $t_{\frac{1}{2}} = 31 \pm 1$ hr).

Counting of the isolated osmium and iridium

In the present work the separated samples of osmium were counted under a thin end-window Geiger-Müller counter (EHM 2/S), with conventional associated electronic equipment. All measured activities were corrected for paralysis, background, and chemical yield. In order to avoid

self-absorption difficulties, the weights of osmium counted from analytical samples and from standards were kept closely similar.

The separated samples of iridium were counted with a NaI(Tl) γ-scintillation counter type 1186A. All measured counting rates were corrected for paralysis, background and chemical yield.

The radiochemical purity of separated osmium and iridium samples was confirmed by decay measurements (*e.g.* see Fig. 1). In the case of iridium, γ-ray spectra were also measured (Fig. 2).

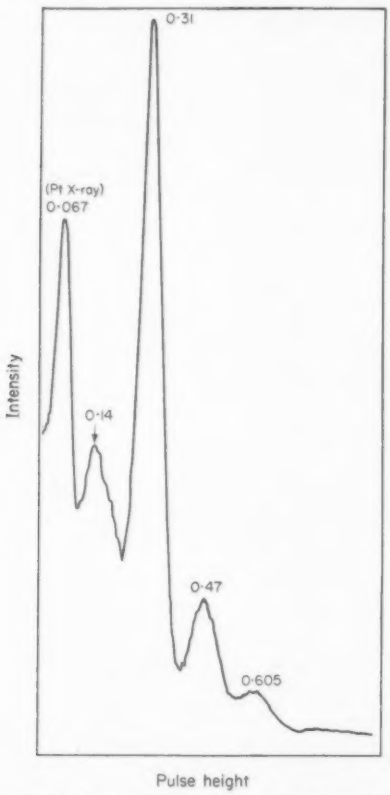


Fig. 2.—γ-Ray spectrum of iridium separated from an analysis sample. Energies in MeV.

RESULTS

In Table II are shown results of analyses of pure samples of palladium and platinum. No osmium or iridium could be detected in these specimens by emission spectrographic analyses.

DISCUSSION

Attention must be given to possible errors caused by conflicting nuclear processes. On neutron-irradiation platinum may give rise to osmium and iridium radio-isotopes by the following nuclear reactions:

$^{196}Pt(n,\alpha)^{193}Os$	(i)	$^{195}Pt(n,p)^{195}Ir$	(v)
$^{194}Pt(n,\alpha)^{191}Os$	(ii)	$^{194}Pt(n,p)^{194}Ir$	(vi)
$^{198}Pt(n,p)^{198}Ir$	(iii)	$^{192}Pt(n,p)^{192}Ir$	(vii)
$^{196}Pt(n,p)^{196}Ir$	(iv)	$^{190}Pt(n,p)^{190}Ir.$	(viii)

TABLE II.—OSMIUM AND IRIDIUM CONTENTS OF SAMPLES OF PALLADIUM AND PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Osmium found, *ppm*	Iridium found, *ppm*
Palladium, Pd 1	0·08 0·08	10·4 10·5 11·1 11·1
Platinum, Pt 1	0·30 0·31 0·34 0·36	0·56 0·45 0·53 0·47
Platinum, Pt 2	0·61 0·55	1·45 1·49 1·46 1·50
Platinum, Pt 3	0·85 1·06 0·96 0·96	0·34 0·34 0·28 0·28
Platinum, Pt 4	0·87 0·82	0·38 0·36 0·32 0·32
Platinum, Pt 5	0·25 0·25	3·47 3·43 3·31 3·27
Platinum, Pt 6	0·03 0·03	0·65 0·59
Platinum, Pt 7	0·23 0·22	0·099 0·097

These nuclear reactions are liable to occur with fast neutrons, of which there is a proportion under the irradiation conditions employed in BEPO and DIDO.

With a knowledge of relevant cross-sections and pile fluxes, the disintegration rate of a given radionuclide formed by a (n,γ), (n,p) or (n,α) reaction can be calculated by means of the following equation:

$$A_\tau = \frac{f\sigma\theta WN}{M}\left[1 - \exp.\left(\frac{-0{\cdot}693t}{t_{\frac{1}{2}}}\right)\right]\exp.\left(\frac{-0{\cdot}693\tau}{t_{\frac{1}{2}}}\right)$$

where

A_τ = disintegration rate at a time τ from the end of irradiation, disintegrations/sec,
f = relevant pile neutron flux, neutrons/cm^2/sec,

W = weight of target element, g,
M = atomic weight of the element,
θ = natural abundance of the particular isotope of the element giving rise to the active species,
σ = activation cross-section (cm^2) of the isotope for the particular nuclear reaction,
N = Avogadro number, $6{\cdot}023 \times 10^{23}$,
t = time of irradiation,
and
$t_{\frac{1}{2}}$ = half-life of radioactive product.

Cross-sections for reactions (i)–(viii) with the pile distribution of neutrons may be calculated by the method of Hughes,[13] but since calculated values are only approximate it was decided to investigate experimentally the interference produced by such reactions.

0·1-g Samples of platinum, Pt 1, were analysed using a thermal neutron flux of 1×10^{12} neutrons/cm^2/sec in BEPO, where the corresponding flux of fast neutrons was $1{\cdot}6 \times 10^{11}$ neutrons/cm^2/sec.[14] The following results were obtained for the apparent osmium and iridium contents: Os 0·35, 0·34, 0·34, 0·39, 0·37, 0·38 ppm; Ir 0·70, 0·73, 0·62, 0·59 ppm. It may be noted that these results are higher than the corresponding values shown in Table II where irradiation in DIDO was used. Since the fast neutron flux under the irradiation conditions in DIDO was *ca.* 5×10^8 neutrons/cm^2/sec,[14] it follows that under the analysis conditions a fast flux of $1{\cdot}6 \times 10^{11}$ neutrons/cm^2/sec may give rise to a spurious osmium content of *ca.* 0·03 ppm and a spurious iridium content of *ca.* 0·16 ppm. With the irradiation conditions employed in DIDO interference due to fast neutron reactions may therefore be ignored.

Further nuclear processes which could possibly interfere with the neutron-activation analysis of osmium [reactions (ix) and (x)] and iridium [reactions (xi)–(xiii)] have been shown by calculation[13,15] to be unimportant in the present work:

$$^{191}\mathrm{Ir(n,p)}^{191}\mathrm{Os} \qquad \text{(ix)}$$

$$^{193}\mathrm{Ir(n,p)}^{193}\mathrm{Os} \qquad \text{(x)}$$

$$^{197}\mathrm{Au(n,\alpha)}^{194}\mathrm{Ir} \qquad \text{(xi)}$$

$$^{190}\mathrm{Os(n,\gamma)}^{191}\mathrm{Os} \xrightarrow{\beta^-} {}^{191}\mathrm{Ir(n,\gamma)}^{192}\mathrm{Ir} \qquad \text{(xii)}$$

$$^{192}\mathrm{Os(n,\gamma)}^{193}\mathrm{Os} \xrightarrow{\beta^-} {}^{193}\mathrm{Ir(n,\gamma)}^{194}\mathrm{Ir}. \qquad \text{(xiii)}$$

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Zusammenfassung—Eine Methode wird beschrieben, um Ultramikromengen von Osmium und Iridium in Proben von Palladium und Platin zu bestimmen. Um Unterschiede in der Selbstabschirmung von Probe und Standard zu vermeiden, wurden kleine Mengen Osmium und Iridium zu den analytischen Proben zugesetzt. Zur Bestrahlung der Palladiumproben wurde der Harwell-Reactor BEPO als Neutronenquelle herangezogen. Um falsche Ergebnisse durch (n,p) und (n,α) Reaktionen zu vermeiden, wurde der Ofen DIDO zur Neutronenaktivierung von Platinproben herangezogen. Jede Bestimmung benötigt 0·1 g Probe. Radiochemische Trennung unter Heranziehung von Trägermethoden wurden Verwendet, um die induzierten-Osmium- und Iridiumaktivitäten zu isolieren.

Ergebnisse für den Osmium und Iridiumgehalte einiger reiner Palladium- und Platinproben werden mitgeteilt.

Résumé—Les auteurs décrivent une méthode de dosage d'ultramicroquantités d'osmium et d'iridium dans des échantillons de palladium et de platine. Afin d'éviter des différences "d'autoprotection" entre les échantillons et les étalons pendant l'irradiation par les neutrons, les étalons ont été préparés par addition de très faibles quantités connues d'osmium et d'iridium aux échantillons analytiques. Dans l'analyse des échantillons de palladium la pile BEPO de Harwell a été utilisée comme source de neutrons. Pour éviter des résultats erronés dus à des réactions (n,p) et (n,α), la pile DIDO a dû être utilisée pour l'activation par les neutrons des échantillons de platine. Chaque dosage nécessitait 0,1 g d'échantillon, et des séparations radiochimiques utilisant des entraîneurs ont été employées pour isoler les activités induites de l'osmium et de l'iridium. Les résultats sont donnés en teneurs en osmium et en iridium des échantillons de palladium et de platine purs.

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ETHANOL-WATER-HYDROCHLORIC ACID ELUENTS IN ANION-EXCHANGE SEPARATIONS

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Summary—A ternary system of ethanol-water hydrochloric acid has been investigated for the anion-exchange separation of elements which have low adsorption coefficients in aqueous hydrochloric acid solutions. A ternary system is used to express the data from batch distribution coefficients in order to facilitate the prediction of column separation. The anion-exchange separation of manganese from nickel and calcium and the separation of yttrium and scandium has been accomplished.

DURING the course of the investigation of the separation of metals by means of the anion-exchange separation of their chloro-complexes, it became apparent that the addition of water-miscible organic solvents enhanced the adsorption of many of these complexes. An extensive study of the adsorption characteristics of ions from aqueous hydrochloric acid solution[1] has led to many anion-exchange separations of metals.[2–6]

The addition of non-aqueous solvents to increase the adsorption has been considered by several investigators.[7–9] In most cases investigations have been confined to elements which show a considerable adsorption from aqueous hydrochloric acid solutions. It appeared more fruitful to utilise the non-aqueous solvents in order to develop anion-exchange separations of those elements which exhibit low distribution coefficients from aqueous solutions. The purpose of this investigation was to extend the use of ion-exchange separations to those elements which show limited adsorption from aqueous solution. For this reason elements such as iron, copper, and cobalt, which are easily adsorbed from aqueous solution, were automatically excluded from the investigation.

EXPERIMENTAL

Reagents

Anion-exchange resin: Dowex 1 × 8, 200–400-mesh chloride-form resin was used for both the equilibrium studies and the column separations. The resin as received was slurried with water and the fines decanted several times. The resin was then loaded in a large plastic column and washed several times with alternate solutions of 9 *M* and 0·5 *M* hydrochloric acid and with 2·5% hydrofluoric acid. This treatment removes metal impurities from the resin. The resin was washed thoroughly with water in order to remove the acid and subsequently oven-dried at 100°.

Metal solutions: The metal chlorides were used in all cases. In some cases it was necessary to convert oxides or other salts to the chlorides before the equilibrium studies or column separations. The metal chlorides were dissolved in water and standardised by EDTA titrations using established techniques. During the course of the investigation of the ethanol-rich regions and particularly the absolute alcohol composition, it was necessary to prepare standard solutions of the metal chlorides in absolute alcohol.

Ethanol-water-hydrochloric acid mixtures: In order to simplify the representation of data and the preparation of various elution mixtures, the solutions were treated as a ternary phase diagram of ethanol-water-hydrochloric acid. Each solution is made up on the basis of twelve parts in order to simplify the use of concentrated hydrochloric acid in the diagram. Thus a 1 *M* solution of hydrochloric acid represents a mixture of one part of concentrated hydrochloric acid and eleven parts of

water and/or ethanol. If two components are specified, a single composition on the ternary is fixed, since the total of parts must equal twelve. In all cases the changes in volume due to mixing are ignored. Admittedly volume changes do take place; however, if one transposes from equilibrium diagrams to column separations and ignores volume changes in both cases, the volume changes which do take place are purely academic.

Measurement of equilibrium coefficients

2·000 ± 0·001 g of dried resin were transferred to 125-ml polyethylene screwcap bottles. The appropriate volumes of sample solution, alcohol, water and hydrochloric acid were added to give a total volume (added) of 120 ml. A minimum ratio of ten to one was maintained between the capacity of the resin and the metal ion added (equivalents), assuming that the adsorbed species was a univalent anion. The bottles were capped slightly below atmospheric pressure by compressing the bottle before tightening the cap, and revolved slowly end-over-end for 12 hr. The polyethylene bottles are convenient for equilibrium studies and by working with a somewhat reduced pressure the danger of losses by leakage is diminished.

After mixing, the contents of the bottle were filtered through a dry filter paper in order to remove the resin, and the metal content of the liquid phase was determined by an EDTA titration of an aliquot. The distribution coefficients D_v were calculated from the formula

$$D_v = \frac{\text{meq metal on resin/ml of resin}}{\text{meq metal in soln/ml of solution}}.$$

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Representation of results

The distribution coefficients obtained from the equilibrium studies can be used to predict the behaviour of species in a column separation. For column separations it is desirable to have widely divergent distribution coefficients for the metal ions to be separated. The ion to be eluted from the column should have a low distribution coefficient in order to be eluted from the column in a reasonable volume. The ion to be retained on the resin should have a large distribution coefficient in order to minimise the possibility of contamination.

In order to correlate the distribution coefficients obtained from the ethanol-water-hydrochloric acid system with the data available from aqueous hydrochloric acid solutions the logarithm of the distribution coefficient was used. If one uses the ternary system of co-ordinates for the composition of the aqueous phase and plots the log of the distribution coefficients perpendicular to the plane of the triangle, a curved surface is obtained from which one can observe the log D_v for any liquid composition in the triangle. In practice this becomes complicated because the over-lapping curved surfaces become difficult to correlate in order to select optimum conditions for a separation. Prior experience has indicated that if log D_v is greater than one the constituent is easily retained on the column, whereas log D_v values 0·5 or less represent ions relatively easy to elute. For this reason it appeared convenient to determine the liquid-phase compositions where log D_v was equal to or greater than one. This was accomplished by obtaining log D_v values at systematic points through the region of the ternary system where adsorption was observed. Log D_v values were obtained with constant parts of alcohol and varying ratios of water-hydrochloric acid. These log D_v values were plotted so as to give the log D_v *vs.* water-hydrochloric acid ratio for any given level of alcohol. From these plots it was possible to obtain the compositions of the liquid phase where log D_v is equal to one. If plotted on the three-dimensional curved surface which represents the log D_v values a curve would result which separates the surface where log D_v is equal to one. The curve so obtained was projected onto the ternary system so as to represent in two dimensions the compositions of the system where log D_v equals one. These curves are shown in Fig. 1.

Areas to the left of a curve represent log D_v greater than one, while areas to the right represent log D_v values less than one. It should be noted that Fig. 1 does not represent the complete ternary system, but the HCl—H_2O line in Fig. 1 is at the six parts of alcohol level. It is apparent that only a small portion of the ternary system provides an adequate distribution coefficient to allow the retention of these ions on a column. However, the metal ions shown in Fig. 1 show little or no adsorption from aqueous hydrochloric acid, so the addition of ethanol to the system has a considerable effect. Ions which exhibit strong adsorption from aqueous hydrochloric acid may be expected to show even stronger adsorption in the ternary system.

In order to utilise Fig. 1 to predict conditions for column separations, it is necessary to select a composition which lies within the area bounded by the log $D_v = 1$ curves. The elements whose curves lie to the left of the composition selected will be eluted while those to the right will be adsorbed. It is preferable to use a composition as far away from the curve for the elements to be eluted as is possible without crossing the curves for the elements to be adsorbed.

In addition to the elements which show significant adsorption, there are some elements which show little adsorption even in the ternary system. For example, nickel, calcium and chromium may be separated from the elements shown in Fig. 1 by selecting a composition in the area to the left of the log $D_v = 1$ curve for the element selected.

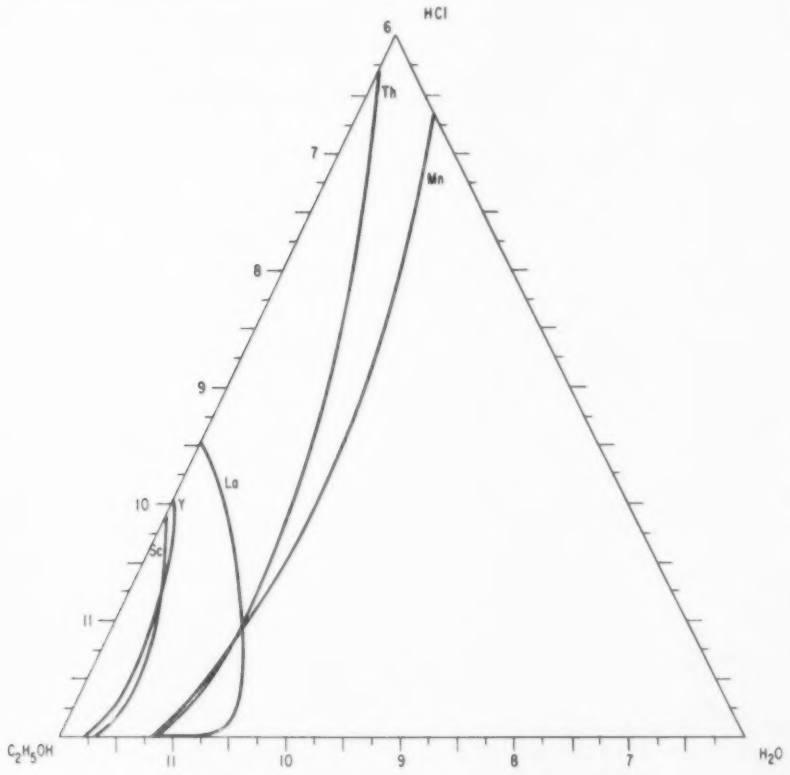

FIG. 1.—Curves of compositions where log D_v is equal to unity.

The adsorption characteristics at the absolute alcohol point are somewhat anomalous and require special mention. In some cases studied a maximum adsorption was noted at a composition near the 11·6 parts of alcohol: 0·2 parts of water: 0·2 parts of hydrochloric acid. The adsorption decreased from this point in all directions. The decrease in adsorption at the absolute alcohol point is particularly interesting in that the changes in the adsorption for yttrium and scandium are sufficiently different to allow a separation. Fig. 1 shows no composition where yttrium and scandium may be separated. The log D_v values are greater than 1, and nearly the same, as one approaches the composition 11·6 parts of alcohol: 0·2 parts of water: 0·2 parts of hydrochloric acid. At the absolute alcohol point scandium shows a sharp decrease in adsorption whereas yttrium shows a sharp increase. In absolute alcohol the log D_v for scandium has decreased from 1·24 to 0·73 while the log D_v for yttrium has increased to a maximum of 2·36. Obviously this difference is adequate for a separation. Thorium, lanthanum and erbium also exhibit a sharp increase at the absolute alcohol point. Manganese decreases similarly to scandium, but the log D_v value remains greater than one.

Column separations

Manganese from nickel or calcium: The columns used contained a resin bed, 1 cm × 10 cm, of Dowex 1 × 8, 200–400 mesh, chloride-form anion-exchange resin. Before introducing the sample solution the resin bed should be equilibrated with the solvent to be used during the elution. The solvent selected for the retention of manganese on the column was 10 parts of ethanol:2 parts of hydrochloric acid which gives a log D_v for manganese of 2·5.

The sample solution of the chlorides was evaporated to a small volume and diluted to 50 ml with the 10:2 solvent. The sample was transferred to a column and nickel or calcium eluted with 100 ml of the 10:2 solvent. Manganese was subsequently eluted with 100 ml of 0·5 *M* hydrochloric acid.

Yttrium from scandium: The columns used contained a resin bed, 6 mm × 47 cm, of Dowex 1 × 8, 200–400 mesh, chloride-form anion-exchange resin. The resin bed was equilibrated with absolute ethanol before adding the sample to the column. The sample solution of the chlorides was evaporated to a small volume and diluted to 50 ml with absolute ethanol. The solution was then transferred to the ion-exchange column. After the solution drained to the resin bed, the scandium was eluted with 150 ml of absolute ethanol. The yttrium was subsequently eluted with 150 ml of 8 parts of ethanol: 2 parts of water: 2 parts of hydrochloric acid.

The determinations were concluded by established EDTA procedures after volatilisation of the solvent.

DISCUSSION

The results which were accumulated in order to construct Fig. 1 were limited to those elements which exhibit limited adsorption in aqueous hydrochloric acid. Elements such as copper, cobalt, iron, zinc, *etc.*, which may be strongly adsorbed under appropriate conditions from aqueous hydrochloric acid solutions would be expected to show strong adsorption over much of the ternary system. Although one could construct curves in Fig. 1 for these elements it appears more convenient to use the alcohol-water-hydrochloric acid system only as an auxiliary technique to the well-established aqueous ion-exchange separations. The separation scheme is intended for further separations of those elements which appear in the 7–9*M* aqueous hydrochloric acid eluents in anion-exchange separations. The eluent should be evaporated to a small volume, then sufficient alcohol, water and hydrochloric acid added to attain the appropriate composition on Fig. 1.

In addition to ethanol one may use other miscible solvents such as acetone and isopropyl alcohol. The characteristics of adsorption are modified to some extent, however; ethanol was satisfactory for the separations desired.

The difference in the adsorption characteristics of lanthanum and yttrium is unusual. The log $D_v = 1$ curve for erbium (not shown) is very close to that of yttrium. An investigation of other members of the lanthanide series will be conducted with the possibility of obtaining some separations of mixtures of the rare earths. In the event that a series of log $D_v = 1$ curves for the other rare earths lie between the lanthanum and erbium lines gradient elution techniques should be applicable for the separation of these elements in a high state of purity.

Further investigation of the nature of the adsorbed species for the absolute alcohol solutions is necessary. Since chloride ions are not added in excess one would assume that the chloride necessary for the formation of chloro complex is furnished by the resin:

$$RR_3'N^+Cl^- + LaCl_3 \rightleftharpoons RR_3'N^+LaCl_4^-.$$

Zusammenfassung—Ein ternäres system Äthanol-Wasser-Salzsäure wurde untersucht um die Trennung von Elementen mittels Anionaustauscher zu verbessern, wenn die Absorptionkoeffizinten in wässriger Salzsäure zu nieder sind. Ein ternäres System wurde herangezogen um die Verteilungskoeffizienten

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auszudrucken, was die Voraussagen über den Wirkungsgrad von Saulentrennungen erleichtert. Trennungen von Mangan von Nickel und Calcium sowie Yttrium von Scandium an Anionenaustauschern wurden ausgearbeitet.

Résumé—Un système ternaire: éthanol-eau-acide chlorhydrique, a été étudié en vue de la séparation par échange anionique d'éléments qui ont de faibles coefficients d'adsorption en solutions aqueuses d'acide chlorhydrique. Un système ternaire est utilisé pour exprimer les résultats à partir des coefficients de partage de l'échantillon afin de faciliter la prévision de la séparation sur colonne. Les séparations par échange anionique du manganèse d'une part et du nickel et du calcium d'autre part, et la séparation de l'yttrium et du scandium, ont été réalisées.

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NON-AQUEOUS SOLVENTS IN ANION-EXCHANGE SEPARATIONS*

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Summary—Distribution coefficients are measured for the partition of metal ions between anion-exchange resin and organic solvent-water mixtures containing hydrochloric acid. The presence of an organic solvent causes metal ions to be taken up at lower hydrochloric acid concentrations. In many cases, distribution coefficients are significantly higher than in water-hydrochloric acid systems. If other conditions are comparable, the order of distribution coefficients in alcohol-water-hydrochloric acid is: isopropyl > ethyl > methyl alcohol. Column separations of metal ion mixtures can be carried out by eluting with alcohol-water-hydrochloric acid mixtures of different compositions. Successful separations of a number of mixtures are reported.

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INTRODUCTION

THE separation of metals as chloro complexes from aqueous hydrochloric acid solutions using anion-exchange columns is now a well-established and valuable analytical procedure.[1–8] In this method, metals that form anionic chloro complexes are taken up from strong hydrochloric acid solutions; other metals pass through the column. Then the metals on the column are eluted one or two at a time using aqueous solutions of hydrochloric acid that are progressively more dilute.

It was observed that metals are taken up strongly and at lower hydrochloric acid concentrations if an appreciable amount of a water-miscible organic solvent is added to the aqueous hydrochloric acid. The purpose of the present work was to study the anion-exchange behaviour of metal chloro complexes in partly non-aqueous media. The primary aim was to find conditions that would improve the convenience and broaden the scope of this type of analytical separation.

Katzin and Gebert[9] studied the absorption of lithium chloride, lithium nitrate, cobalt chloride and nickel nitrate on chloride- and nitrate-form anion-exchange resins from acetone solution. They noted that the whole salt is adsorbed and suggested that the salts might be taken up as complex anions. On the other hand, Davies and Owen[10] postulated that the salts are adsorbed by the resin by a solvent extraction process. Tuck and Welch[11] found that the uptake of plutonium^{IV} by an anion-exchange resin from a nitric acid-diethyleneglycoldibutyl ether solution is the result of anionic complex formation.

In the anion-exchange separation of sulphate, sulphite, thiosulphate, sulphide, selenite and tellurite, Iguchi[12,13] found that the addition of alcohol to the eluting agent increased the adsorbabilities of all but the selenite and tellurite. Burstall *et al.*[14] eluted gold (adsorbed as the cyanide) from an anion-exchange column using an acetone eluent containing 5% hydrochloric acid and 5% water. Korkisch *et al.*[15] separated uranium^{VI} from certain other metals on a chloride-form anion-exchange

* Contribution No. **921**. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

column using a solution of hydrochloric acid in mixed water and ethyl alcohol. The addition of 10 to 25% methyl alcohol to an aqueous hydrochloric acid eluent has been found to improve the anion-exchange separation of zinc and cadmium.[16] Recently Kojima[17,18] and Yoshino and Kurimura[19] studied the anion-exchange behaviour of several of the transition elements in mixed solvents containing hydrochloric acid. Distribution coefficients of metal ions were measured in various combinations of hydrochloric acid, water and organic solvent, and the results were compared with the distribution coefficients found in aqueous hydrochloric acid solutions by Kraus and Nelson.[1,2] In all cases the incorporation of a non-aqueous solvent in the mixture caused the distribution coefficients to be higher. An elution scheme for several metal ions was devised, and the method was applied to the determination of aluminum and copper in certain zinc alloys.

EXPERIMENTAL

Reagents

Anion-exchange resin: Dowex 1 × 8 "analysed reagent" resin, either 100- to 200-mesh or 200- to 400-mesh. The finer mesh resin gives somewhat sharper separations and was used in most of the column separations. Before use, backwash the resin to remove the very fine particles, then wash a column of resin with 2 to 2·5*M* perchloric acid to remove metallic impurities. Wash with water, then convert the resin to the chloride-form by successive washing with 2 to 2·5*M*, 1*M*, and 0·005*M* hydrochloric acid. Wash with water, then remove the water by suction filtration. Wash the resin with absolute alcohol, then with acetone, and allow it to air-dry. The air-dried resin has a water content of 5 to 10% by weight.

EDTA, (disodium dihydrogen ethylenediaminetetra-acetate dihydrate): Prepare a 0·05*M* stock solution from reagent-grade salt. Standardise by titration of zinc^{II} from primary standard zinc metal or by titration of cadmium^{II} from the primary standard, HCdV.[20] Naphthyl azoxine indicator is recommended for the standardisation.[20,21]

Metal salts: Reagent grade metal chlorides were used when available. Rare-earth, yttrium and scandium chloride solutions were prepared by dissolving the oxides in hydrochloric acid. Thorium^{IV} and uranium^{VI} nitrates, which were converted to chlorides by anion-exchange, were used, and vanadium^{IV} was used as the sulphate. In a few experiments metal perchlorates were employed. The solutions were 0·05*M* to 0·1*M*.

Organic solvent-water-hydrochloric acid mixtures: Mixtures were prepared so that the amount of organic solvent and water was expressed as percentage by volume and the hydrochloric acid concentration as molarity. For example, 1 litre of 1*M* hydrochloric acid in 80% isopropyl alcohol is prepared as follows: Mix together 800 ml of isopropyl alcohol, 83 ml of concentrated hydrochloric acid and 117 ml of water. Disregard any changes in volume due to mixing.

Procedures

Macro amounts of most metal ions were determined by titration with EDTA. Conditions are summarised in Table I. Iron^{III}, chromium^{III} and uranium^{VI} were determined by standard redox methods.

Micro amounts of metal ions were determined by colorimetric methods: copper^{II} with neocuproïne,[28] zinc^{II} with zincon,[29] thorium^{IV} with thorin,[30] uranium^{VI} with arsenazo,[31] bismuth^{III} with thiourea,[32] and iron^{II} with 1:10-phenanthroline.[33]

Measurement of distribution coefficients

Weigh accurately approximately 1 g of air-dried anion-exchange resin into a 125-ml glass-stoppered Erlenmeyer flask. Pipette into the flask 4 ml of metal salt solution and 50 ml of the appropriate organic solvent-water-hydrochloric acid mixture. Stopper the flask and shake for 12 to 18 hr (80% or less of organic solvent) or 22 to 32 hr (more than 80% organic solvent) at 24° ± 1°. Pipette an aliquot from the supernatant liquid, evaporate the acid and organic solvent, and determine the metal ion content by an appropriate analytical method. Determine accurately the water content of the resin and calculate the distribution coefficients on a dry weight basis.

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TABLE I.—TITRATION OF METAL IONS WITH EDTA

Ions titrated	pH	Indicator	Reference
Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}	5.5–6·5	Naphthyl azoxine	21
Mn^{2+}	10	Eriochrome Black T	22
VO^{2+}	5·5–6·5	Naphthyl azoxine (back-titrated with Zn^{2+})	23
Rare earth^{3+}, Y^{3+}	5·5–6·5	Arsenazo	24
Th^{4+}	1·7–3·0	Arsenazo	24
Sc^{3+}	3·0–4·5	Methylthymol blue	22
Bi^{3+}	1·3–2·0	Thiourea	25
Zr^{4+}	1·3–2·0	Thiourea (back titrated with Bi^{3+})	26
Ca^{2+}	10	Thymolphthalexone	27
Mg^{2+}	10	Eriochrome Black T	22

Separation of mixtures

Prepare a sample mixture by pipetting into a beaker known amounts of standard metal salt solutions. Carefully evaporate the sample mixture nearly to dryness. Add 5 ml of 0·3*M* hydrochloric acid in 97% ethyl alcohol. When the residue is dissolved, transfer the sample to an anion-exchange column using 0·3*M* hydrochloric acid in 95% ethyl alcohol as a rinse solution. Use an ion-exchange column having an inside diameter of either 12 mm or 22 mm; the height of Dowex 1 × 8 resin bed for various separations is indicated in Tables II, III, IV. Elute the various sample constituents from the column with the types and quantities of eluent indicated in Tables II, III, IV with a flow rate of 0·25 to 0·33 ml/min. Evaporate the effluent fractions collected, and determine the amount of metal salt present in each effluent fraction by an appropriate titrimetric procedure.

MEASUREMENT OF DISTRIBUTION COEFFICIENTS

Measurement of distribution coefficients of various metal ions over a wide range of conditions is a good way to avoid choosing eluting conditions for column separations by a strictly trial and error method. The batch distribution coefficient, D, is defined:

$$D = \frac{\text{mequiv. metal on resin/g of dry resin}}{\text{mequiv. metal in solution/ml of solution}}$$

Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behaviour for metals eluted from an ion-exchange column. To separate two substances, conditions should be selected such that the distribution coefficient of one is low (preferably 1 or less) so that elution from the column will be rapid. The distribution coefficient of the other substance under the same conditions should be as large as possible so that this substance will be tightly held by the column.

In aqueous hydrochloric acid solution, the distribution coefficient of most metal ions in contact with anion-exchange resin increases as the concentration of hydrochloric acid is increased. After a certain concentration of hydrochloric acid is attained, the distribution coefficient remains about the same or decreases somewhat with further increases in hydrochloric acid concentration. In partly non-aqueous solutions of hydrochloric acid, two factors cause an increase in the value of D; an increase in hydrochloric acid concentration, or an increase in the proportion of non-aqueous solvent in the water-non-aqueous solvent mixture. In solvent mixtures containing an appreciable amount of non-aqueous solvent, a D value sufficiently high to assure quantitative uptake of a substance on an ion-exchange column occurs at a much

lower hydrochloric acid concentration than in completely aqueous systems. Also, the maximum distribution coefficient obtainable in partly non-aqueous systems containing hydrochloric acid is frequently much higher than is possible in aqueous hydrochloric acid solutions. The distribution of manganese^{II} between chloride-form anion-exchange resin and hydrochloric acid solution is an outstanding illustration of the latter. In aqueous hydrochloric acid, the distribution coefficient is always less than 10; in alcohol-hydrochloric acid systems containing only a little water a distribution coefficient of several thousand can be realised.

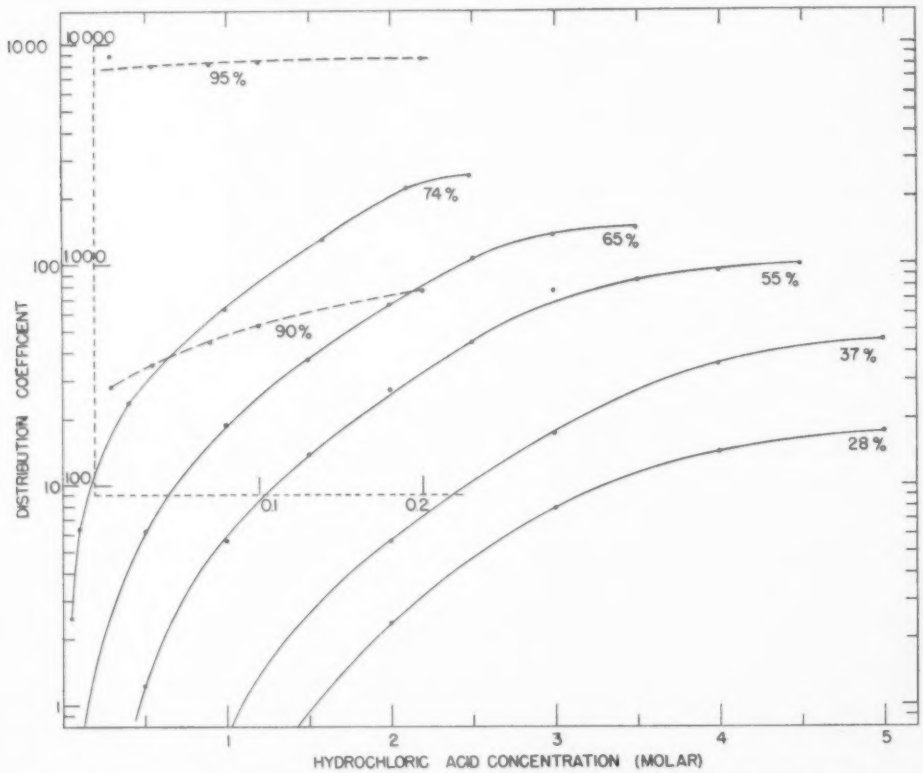

FIG. 1—Distribution coefficients of copper^{II} chloride in various concentrations of isopropyl alcohol *vs.* hydrochloric acid concentrations.

In Fig. 1 the distribution coefficient for copper^{II} is plotted as a function of hydrochloric acid concentration at several isopropyl alcohol-water solvent compositions. It will be noted that the presence of an increasing proportion of isopropyl alcohol has a pronounced effect on the distribution coefficient. In Figs. 2–5, distribution coefficients of other metals are plotted as a function of hydrochloric acid for solvents containing different percentages of isopropyl alcohol.

The effect of different organic solvents on the ion-exchange behaviour of various metal ions was studied. Fig. 6 shows that the various organic solvents studied have about the same effect on the distribution coefficients for copper when the solvent contains an appreciable proportion of water. However, when the solvent contains less than 10 or 15% water, the difference in D in changing from one organic solvent to

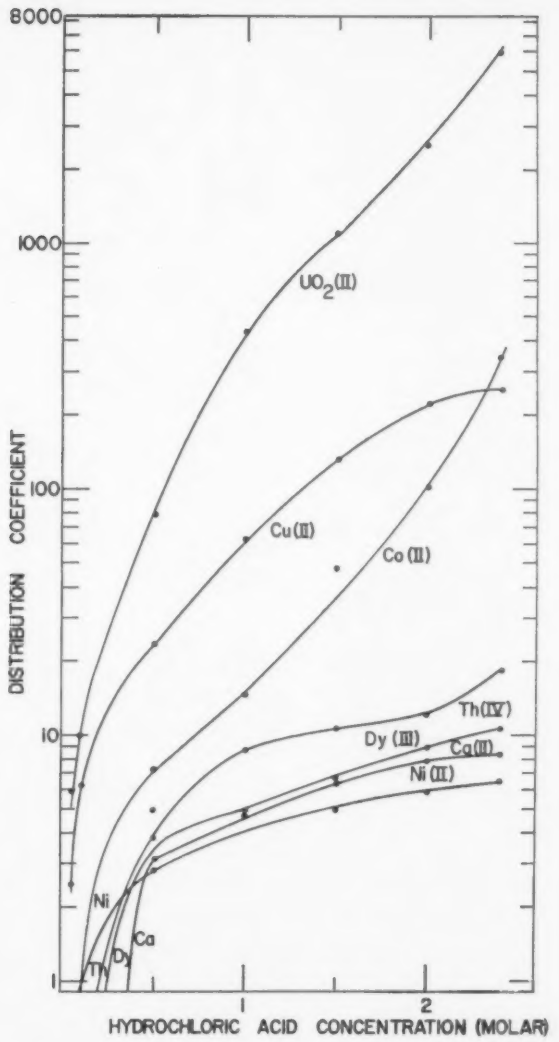

FIG. 2—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 74% isopropyl alcohol.

another is more pronounced. The distribution coefficients of copper as a function of hydrochloric acid concentration for several solvents are plotted in Fig. 7. Distribution coefficients for several metal ions are plotted in isopropyl alcohol, ethyl alcohol and methyl alcohol in Figs. 8–10. In Figs. 11 and 12, distribution coefficients for various metals are plotted as a function of ethyl alcohol concentration for solutions that are 0·3*M* in hydrochloric acid.

In these figures the concentration of hydrochloric acid is kept low for two reasons. When the proportion of non-aqueous solvent in the mixture is high, only a low concentration of hydrochloric acid is required for metals that form chloro complexes to have high distribution coefficients. Also, the use of much higher concentrations of

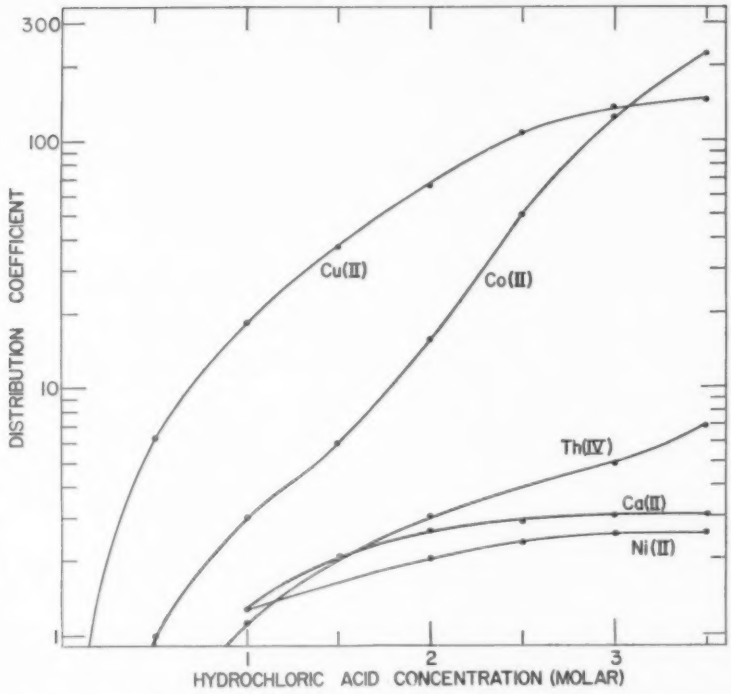

FIG. 3—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 65% isopropyl alcohol.

hydrochloric acid would make it impossible to maintain the desired concentration of non-aqueous solvent and still use concentrated aqueous hydrochloric acid in preparing the solvent mixture.

Figs. 8–10 show that the distribution coefficients of the metal ions studied are higher in ethyl alcohol than in methyl alcohol, and are still higher in isopropyl alcohol. By mixing the alcohols in varying proportions and keeping the hydrochloric acid concentration constant, a gradual transition of D values from one pure alcohol to another is possible. Figs. 13 and 14 show the distribution coefficients for several metal chlorides in methyl alcohol-isopropyl alcohol and methyl alcohol-ethyl alcohol, respectively.

SEPARATIONS

The batch distribution coefficient, D, can be used to calculate the volume of eluting agent required to elute a metal ion from a given ion-exchange column. The relationships used in such a calculation are as follows:

$$D = D \times \frac{\text{g of resin}}{V}$$

$$U^* = V(D_v + 1)$$

where D is the batch distribution coefficient, D_v is a volume distribution coefficient, V is the interstitial volume (ml) of the resin bed, and U^* is the volume (ml) of eluent required to elute a metal ion to a point where the effluent from the column has the

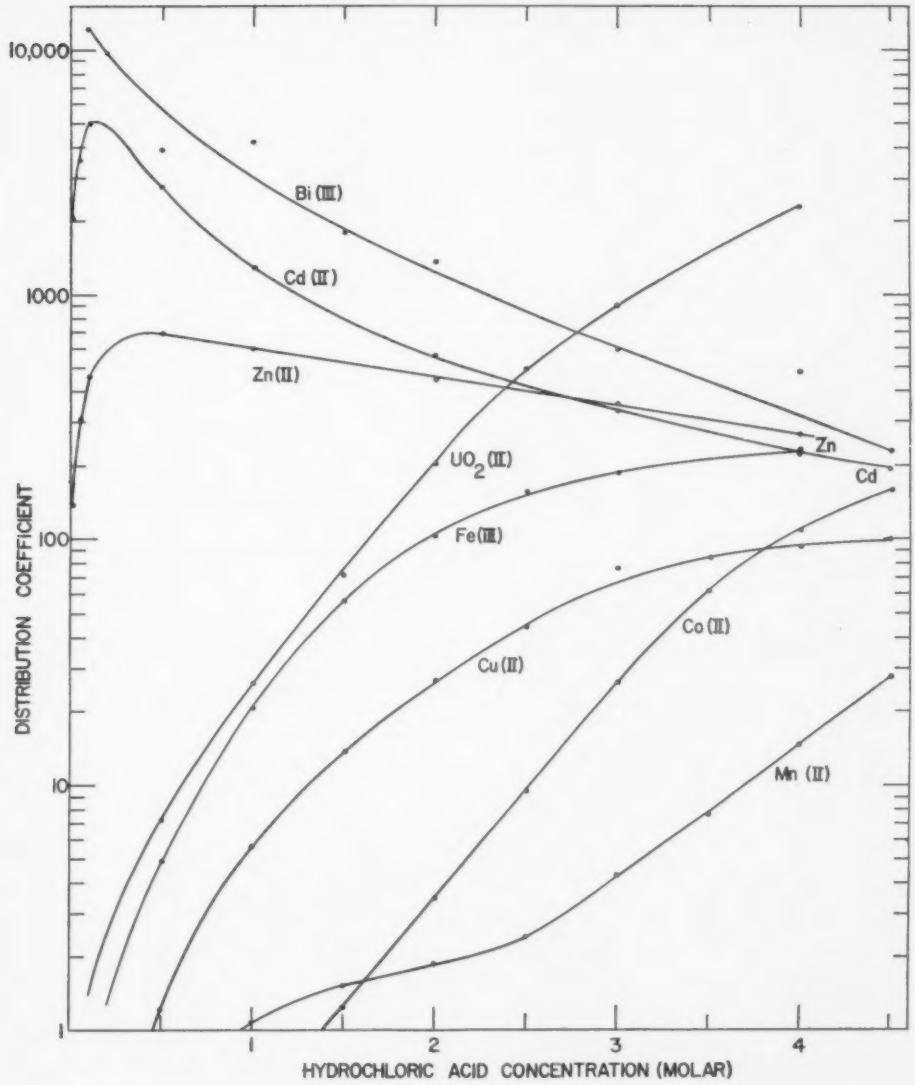

FIG. 4—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 55% isopropyl alcohol. High adsorption group.

maximum concentration in the metal ion eluted. The volume of eluent required to elute *all* of a metal ion depends on the band width of the metal ion eluted. A good discussion of the selection of column dimensions and operating conditions, when the distribution coefficients of the substances to be separated are known, is given by Cornish.[34]

In the present work, batch distribution coefficients served as a valuable guide in selecting conditions for column separations. However, the volume of solution required to elute various ions from a column was always determined by collecting actual fractions from a column and analysing the fractions. Under the conditions used, this

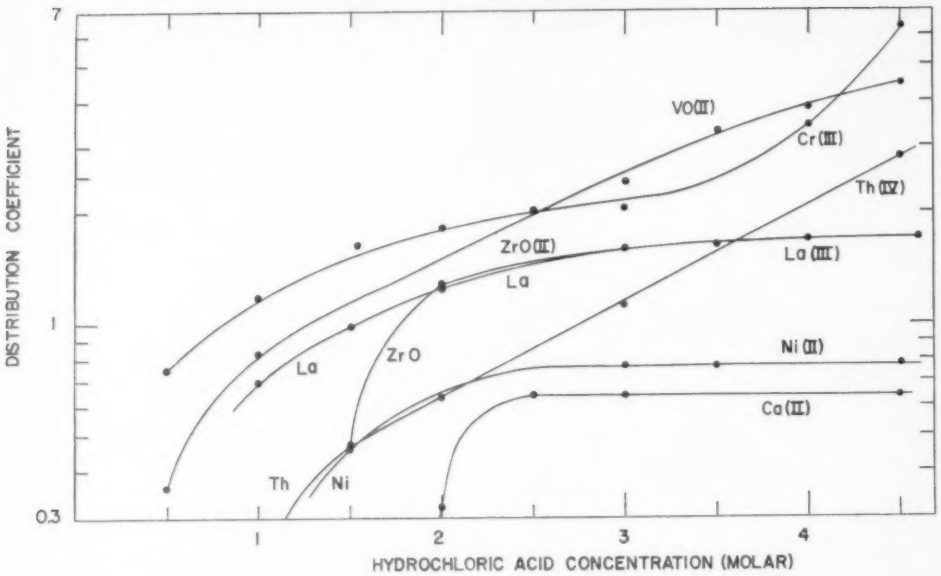

FIG. 5—Distribution coefficients of metal chlorides *vs.* hydrochloric acid concentration in 55% isopropyl alcohol. Low adsorption group.

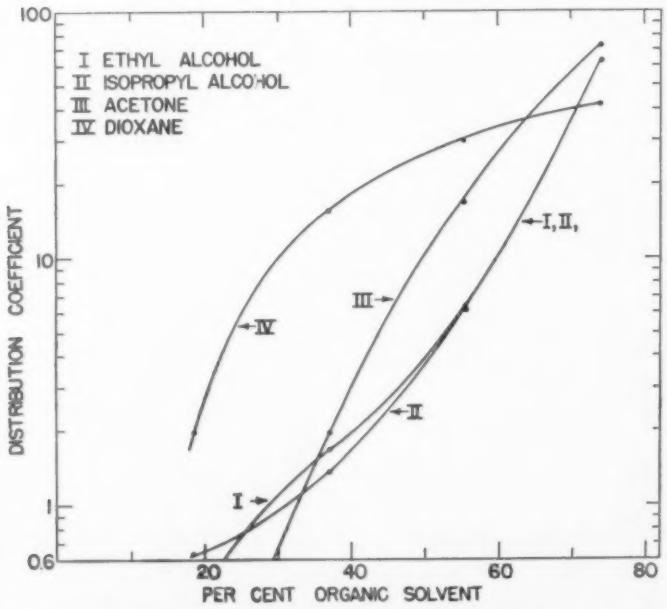

FIG. 6—Distribution coefficients of copper^{II} chloride in 1*M* hydrochloric acid *vs.* varying percentage of organic solvent.

was found to be much more reliable than simply calculating the required volume of eluent from the distribution coefficients.

To separate two metal ions on an anion-exchange column, a solvent composition and hydrochloric acid concentration is chosen such that one metal will be rapidly

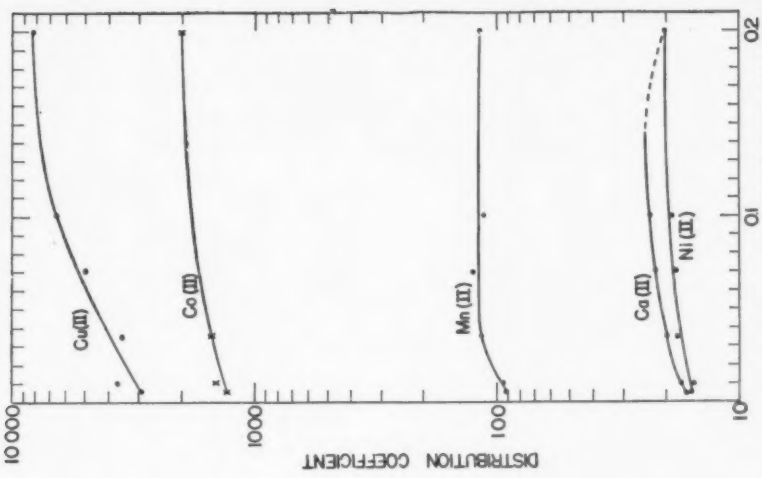

FIG. 8—Distribution coefficients of some metal ions in 96% isopropyl alcohol *vs.* hydrochloric acid concentration.

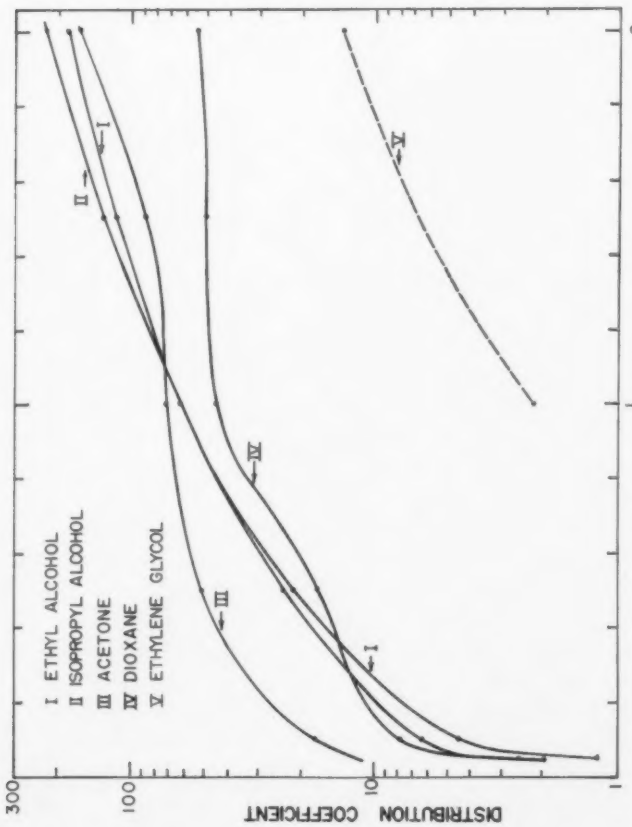

FIG. 7—Distribution coefficients of copper^{II} chloride in 74% organic solvent *vs.* hydrochloric acid concentration.

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eluted from the column (D should be low, preferably 1 or below) while the other metal ion has a high D and is tightly held by the column. When several metal ions are to be separated from each other, the scheme is to choose different conditions for successive elutions so that only one metal ion is eluted by each eluting agent. In selecting the composition of eluting agent, we have three variables to work with: the non-aqueous solvent, concentration of non-aqueous solvent in the non-aqueous-water mixture, and concentration of hydrochloric acid.

In alcohol-water mixtures containing a high proportion of alcohol, only a low concentration of hydrochloric acid is required for metal ions to be strongly taken up by an anion-exchange column. As shown in Figs. 7–10 the distribution coefficients of most metals change little with moderate changes in hydrochloric acid concentration. However, inspection of Figs. 11 and 12 reveals that changes in the alcohol content of the solvent affect the D values of metal ions to varying degrees. Thus one elution scheme is based on the use of a series of eluents with a constant hydrochloric acid concentration (0·3*M*), but with decreasing proportions of alcohol. Ethyl alcohol was chosen because the D values of the "non-adsorbable" metal ions such as nickel^{II} and calcium^{II} are too high in isopropyl alcohol (see Fig. 8). Methyl alcohol was not chosen because D values for "adsorbable" metal ions are significantly lower than in ethyl alcohol (Figs. 9 and 10).

The ethyl alcohol elution scheme is as follows:
Sample is added to column in 95% ethyl alcohol-0·3*M* HCl.
Ni^{II} is eluted with 82% to 95% ethyl alcohol-0·3*M* HCl.
Mn^{II} is eluted with 72% to 82% ethyl alcohol-0·3*M* HCl.
Co^{II} is eluted with 72% ethyl alcohol-0·3*M* HCl.
Cu^{II} and Fe^{III} are eluted with 40% ethyl alcohol-0·3*M* HCl.
Zn^{II} is eluted with 0·005*M* aqueous HCl.

Examples of quantitative column separations using this scheme are given in Table II. In some instances the composition of the sample was such that the elution of one of the sample constituents could be accomplished using a lower concentration of ethyl alcohol than stated in the preceding scheme.

Several separations are not possible using this elution scheme. Uranium^{VI}, copper^{II} and iron^{II} can be separated only as a group. Nickel^{II}, calcium^{II}, vanadium^{IV} and chromium^{III} can also be separated only as a group. Manganese^{II} can be separated from this latter group, but the separation is lengthy and only moderately successful. Separation of manganese^{II} from cobalt is not possible.

At higher ethyl alcohol concentrations, tailing of the elution bands is a problem. Tailing of nickel^{II} when eluted with 0·3*M* hydrochloric acid in 95% ethyl alcohol is particularly bad. When nickel is eluted with 0·3*M* hydrochloric acid-82% ethyl alcohol, the tailing is lessened but is still something of a problem. An attempt was made to eliminate tailing by making the 0·3*M* alcoholic solution of hydrochloric acid up to 0·1*M* in perchloric acid. This speeded up all elutions and diminished tailing of the nickel somewhat, but the over-all improvement was not sufficient to recommend the use of perchloric acid in the eluents.

Another elution scheme uses isopropyl alcohol instead of ethyl alcohol (see Figs. 2–5). In this method the isopropyl alcohol concentration is held constant at 55%, and the concentration of hydrochloric acid is varied. The elution scheme is as follows: Sample is added to the column in 0·3*M* HCl-95% ethyl alcohol.

TABLE II.—SEPARATION AND ANALYSIS OF SYNTHETIC METAL ION MIXTURES ON DOWEX 1 × 8, 200- TO 400-MESH, CHLORIDE-FORM RESIN. METALS APPEAR IN THE ORDER OF ELUTION WITH THE AMOUNT OF WASH SOLUTION INCLUDED WITH THE FIRST ELUTED METAL.

Metal mixture (column dimensions) and eluting agent	Taken, *mg*	Found, *mg*
Ni^{II}-Cu^{II} (3 × 1·1 cm)		
Ni 22 ml 95% EtOH-0·3*M* HCl		
10 ml 74% EtOH-0·3*M* HCl	7·17	7·17
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·01
Ni^{II}-Cu^{II}-Zn^{II} (3 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
9 ml 74% EtOH-0·3*M* HCl	7·17	7·17
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·02
Zn 40 ml 0·005*M* aqueous HCl	7·15	7·16
Mn^{II}-Cu^{II} (3 × 1·1 cm)		
Mn 2 ml 95% EtOH-0·3*M* HCl		
11 ml 74% EtOH-0·3*M* HCl	7·16	7·13
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·02
Ni^{II}-Mn^{II}-Cu^{II} (3 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
41 ml 95% EtOH-0·3*M* HCl	7·17	7·11
Mn 10 ml 72% EtOH-0·3*M* HCl	7·16	7·12
Cu 25 ml 0·005*M* aqueous HCl	7·07	7·02
Ni^{II}-Co^{II} (6 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
13 ml 82% EtOH-0·3*M* HCl	7·17	7·23
Co 15 ml 40% EtOH-0·3*M* HCl	7·64	7·62
Ni^{II}-Co^{II}-Cu^{II}-Zn^{II} (6 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
12 ml 82% EtOH-0·3*M* HCl	7·17	7·20
Co 17 ml 72% EtOH-0·3*M* HCl	7·64	7·62
Cu 15 ml 40% EtOH-0·3*M* HCl	7·07	7·04
Zn 40 ml 0·005*M* aqueous HCl	7·15	7·20
Co^{II}-Fe^{III} (3 × 1·1 cm)		
Co 2 ml 95% EtOH-0·3*M* HCl		
10 ml 72% EtOH-0·3*M* HCl	7·64	7·62
Fe 23 ml 40% EtOH-0·3*M* HCl	6·90	6·92
Ni^{II}-Co^{II}-Fe^{III}-Zn^{II} (6 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
13 ml 82% EtOH-0·3*M* HCl	7·17	7·21
Co 15 ml 70% EtOH-0·3*M* HCl	7·60	7·63
Fe 20 ml 40% EtOH-0·3*M* HCl	6·90	6·90
Zn 40 ml 0·005*M* aqueous HCl	6·91	6·82
Ni^{II}-Fe^{III}-Bi^{III} (3 × 1·1 cm)		
Ni 2 ml 95% EtOH-0·3*M* HCl		
6 ml 72% EtOH-0·3*M* HCl	7·17	7·17
Fe 12 ml 40% EtOH-0·3*M* HCl	6·90	6·88
Bi 25 ml 1*M* aqueous H_2SO_4	6·90	6·82

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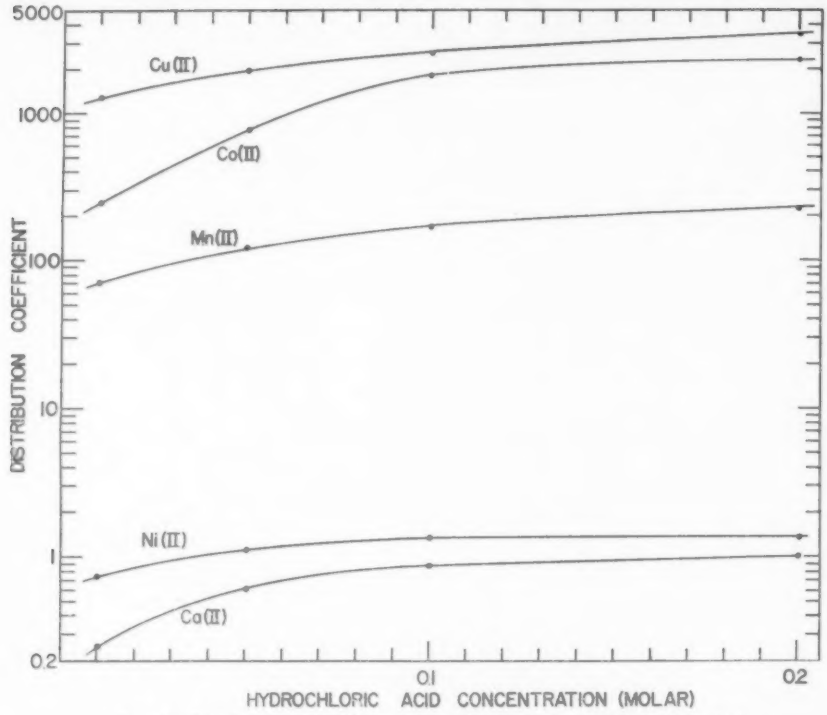

FIG. 9—Distribution coefficients of some metal ions in 96% ethyl alcohol *vs.* hydrochloric acid concentration.

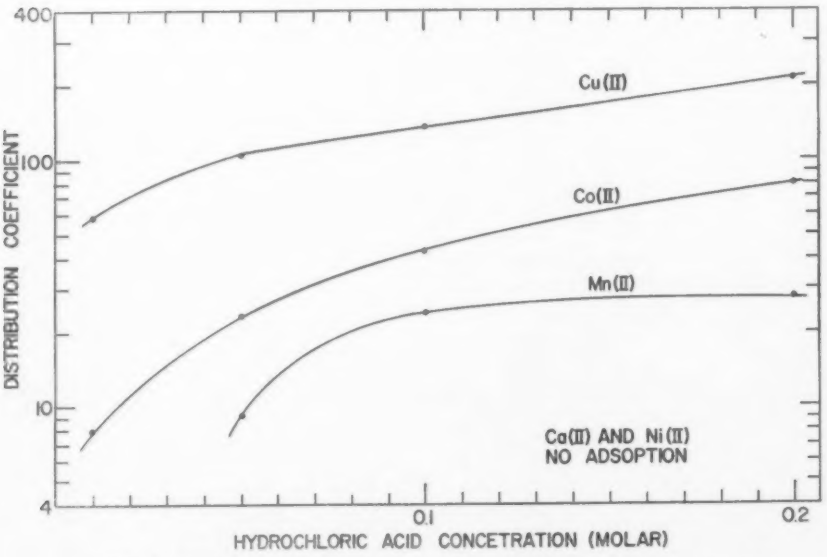

FIG. 10—Distribution coefficients of some metal ions in 96% methyl alcohol *vs.* hydrochloric acid concentration.

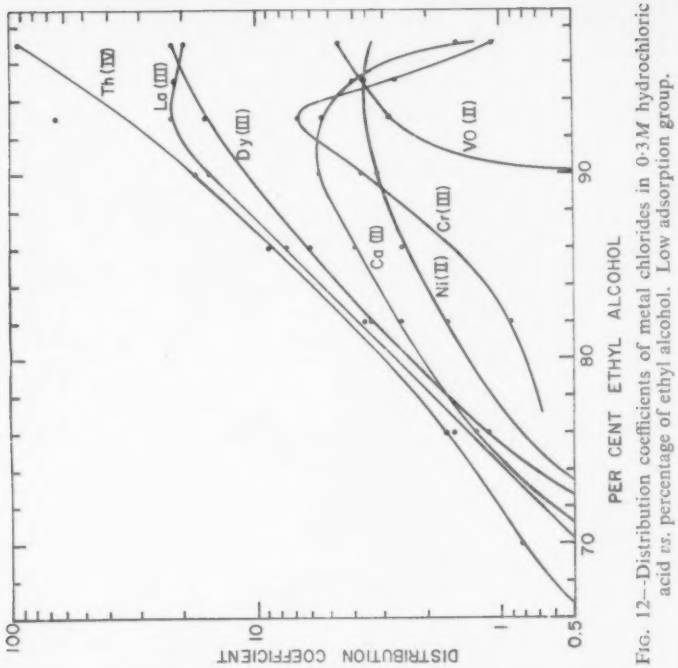

FIG. 12—Distribution coefficients of metal chlorides in 0·3*M* hydrochloric acid *vs.* percentage of ethyl alcohol. Low adsorption group.

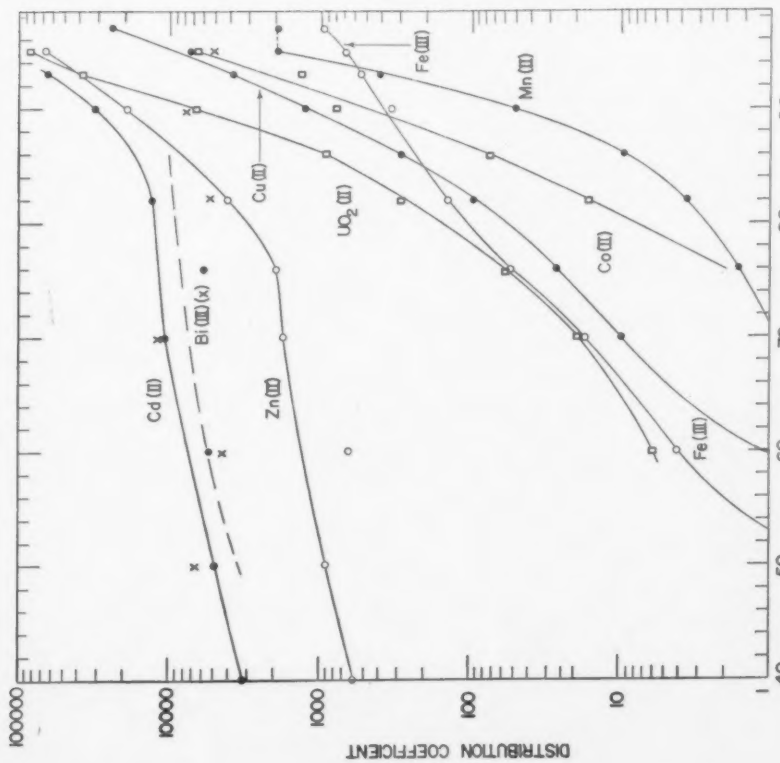

FIG. 11—Distribution coefficients of metal chlorides in 0·3*M* hydrochloric acid *vs.* percentage of ethyl alcohol. High adsorption group.

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Ni^{II}, Mn^{II}, Ca^{II} and Dy^{III} are eluted with 3*M* HCl-55% isopropyl alcohol.
Co^{II} is eluted with 1·3*M* HCl-55% isopropyl alcohol.
Cu^{II} and Fe^{III} are eluted with 0·1*M* HCl-55% isopropyl alcohol.
Zn^{II} is eluted with 0·005*M* aqueous HCl, or Bi^{III} is eluted with 1*M* aqueous sulphuric acid.

TABLE III.—SEPARATION AND ANALYSIS OF SYNTHETIC METAL ION MIXTURES ON DOWEX 1 × 8, 200- TO 400-MESH, CHLORIDE-FORM RESIN. METALS APPEAR IN THE ORDER OF ELUTION WITH THE AMOUNT OF WASH SOLUTION INCLUDED WITH THE FIRST ELUTED METAL.

Metal mixtures (column dimensions) and eluting agent		Taken, *mg*	Found, *mg*
Ni^{II}-Fe^{III}-Bi^{III} (6 × 2·2 cm)			
Ni	4 ml 95% EtOH-0·3*M* HCl		
	50 ml 96% MeOH-0·2*M* HCl	8·96	8·93
Fe	45 ml 0·1*M* HCl-55% 2-PrOH	9·13	9·13
Bi	90 ml 1*M* aqueous H_2SO_4	8·66	8·50
Co^{II}-Fe^{III} (6 × 2·2 cm)			
Co	4 ml 95% EtOH-0·3*M* HCl		
	60 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·58
Fe	45 ml 0·1*M* HCl-55% 2-PrOH	9·13	9·12
Ni^{II}-Mn^{II}-Cu^{II} (6 × 2·2 cm)			
Ni	8 ml 95% EtOH-0·3*M* HCl		
	47 ml 96% MeOH-0·2*M* HCl	8·96	8·94
Mn	80 ml 3*M* HCl-55% 2-PrOH	8·96	9·00
Cu	50 ml 0·1*M* HCl-55% 2-PrOH	8·94	8·89
Ni^{II}-Mn^{II}-Co^{II}-Cu^{II}-Zn^{II} (6 × 2·2 cm)			
Ni	8 ml 95% EtOH-0·3*M* HCl		
	47 ml 96% MeOH-0·2*M* HCl	8·96	8·99
Mn	80 ml 3*M* HCl-55% 2-PrOH	8·96	8·88
Co	70 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·50
Cu	50 ml 0·1*M* HCl-55% 2-PrOH	8·94	8·88
Zn	60 ml 0·005*M* aqueous HCl	8·95	9·06
Ni^{II}-Co^{II}-Cu^{II}-Bi^{III} (6 × 2·2 cm)			
Ni	8 ml 95% EtOH-0·3*M* HCl		
	47 ml 96% MeOH-0·2*M* HCl	8·96	9·06
Co	65 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·51
Cu	40 ml 0·1*M* HCl-55% 2-PrOH	8·95	8·97
Bi	85 ml 1*M* aqueous H_2SO_4	8·66	8·54
Dy^{III}-Mn^{II}-Cu^{II}-Fe^{III}-Bi^{III} (6 × 2·2 cm)			
Dy	8 ml 95% EtOH-0·3*M* HCl		
	47 ml 96% MeOH-0·2*M* HCl	9·22	9·28
Mn	80 ml 3*M* HCl-55% 2-PrOH	8·96	8·99
Cu-Fe[a]	50 ml 0·1*M* HCl-55% 2-PrOH		
	Cu	8·94	9·06
	Fe	9·13	9·06
Bi	85 ml 1*M* aqueous H_2SO_4	8·66	8·66

TABLE III. (*contd.*)

Metal mixtures (column dimensions) and eluting agent		Taken, *mg*	Found, *mg*
Ni^{II}-Th^{IV}-Mn^{II}-Co^{II}-Cu^{II}-Fe^{III} (6 × 2·2 cm)			
Ni	8 ml 95% EtOH-0·3*M* HCl		
	73 ml 48% EtOH-48%*M* OH		
	0·2*M* HCl	8·96	8·99
Th	85 ml 96% MeOH-0·2*M* HCl	9·06	9·06
Mn	85 ml 3*M* HCl-55% 2-PrOH	8·95	8·96
Co	55 ml 1·3*M* HCl-55% 2-PrOH	9·51	9·56
Cu-Fe[a]	50 ml 0·1*M* HCl-55% 2-PrOH		
	Cu	8·94	8·96
	Fe	9·13	9·03
Ca^{II}-Mn^{II} (5 × 2·2 cm)			
Ca	2 ml 95% EtOH-0·3*M* HCl		
	56 ml 96% MeOH-0·2*M* HCl	8·33	8·40
Mn	80 ml 3*M* HCl-55% 2-PrOH	9·06	9·02
Ni^{II}-Mn^{II} (5 × 2·2 cm)			
Ni	2 ml 95% EtOH-0·3*M* HCl		
	56 ml 96% MeOH-0·2*M* HCl	4·45	4·51
Mn	80 ml 3*M* HCl-55% 2-PrOH	9·05	9·07

[a] Cu-Fe eluted together and analysed by a photometric titration[35] with EDTA as titrant.

This scheme gives sharp separations and virtually eliminates tailing of the bands. In Fig. 15 the elution curves are compared for the separation of nickel^{II} and cobalt^{II} by the isopropyl alcohol and the previous ethyl alcohol elution schemes. In the ethyl alcohol scheme, elution with 0·3*M* hydrochloric acid in 82% ethyl alcohol was continued after elution of the nickel until the cobalt break-through. In the isopropyl alcohol scheme, elution with 3*M* hydrochloric acid in 55% isopropyl alcohol was discontinued shortly after elution of the nickel was complete. At this point the cobalt band was still 4 cm from the bottom of the column, and the estimated cobalt break-through with the 3*M* eluent would be around 250 ml.

The isopropyl alcohol scheme does not offer a convenient separation of nickel^{II} or calcium^{II} from manganese^{II}. However, it was found that an excellent separation of nickel^{II} and manganese^{II} can be achieved through the use of 0·2*M* hydrochloric acid in 96% methyl alcohol (see Fig. 10). Although the distribution coefficient for manganese^{II} is only 27 in 0·2*M* hydrochloric acid-96% methanol (compared to a D of around 2000 in 0·3*M* hydrochloric acid-95% ethyl alcohol), column experiments showed that manganese^{II} is still strongly retained by a column. An elution curve for the column separation of nickel^{II} and manganese^{II} is given in Fig. 16. The curve shows sharp bands with very little tailing, and an excellent separation factor.

The recommended separation method is first to separate nickel^{II}, calcium^{II} or dysprosium^{III} from manganese^{II} (and other metal ions) using 0·2*M* hydrochloric acid in 96% methyl alcohol. The metal ions remaining on the column are then separated using the 55% isopropyl alcohol scheme outlined above. Fig. 17 shows elution curves for a multi-component mixture separated by this method, and Table III presents results

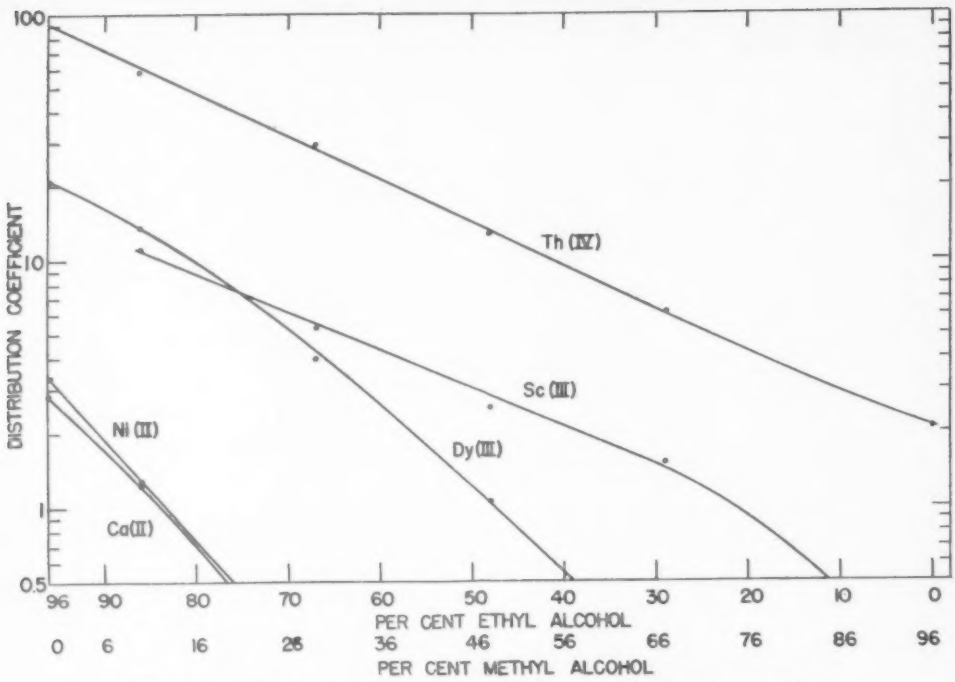

FIG. 13—Distribution coefficients of metal chlorides in 0·2*M* hydrochloric acid *vs.* concentration of methyl alcohol and ethyl alcohol totalling 96%.

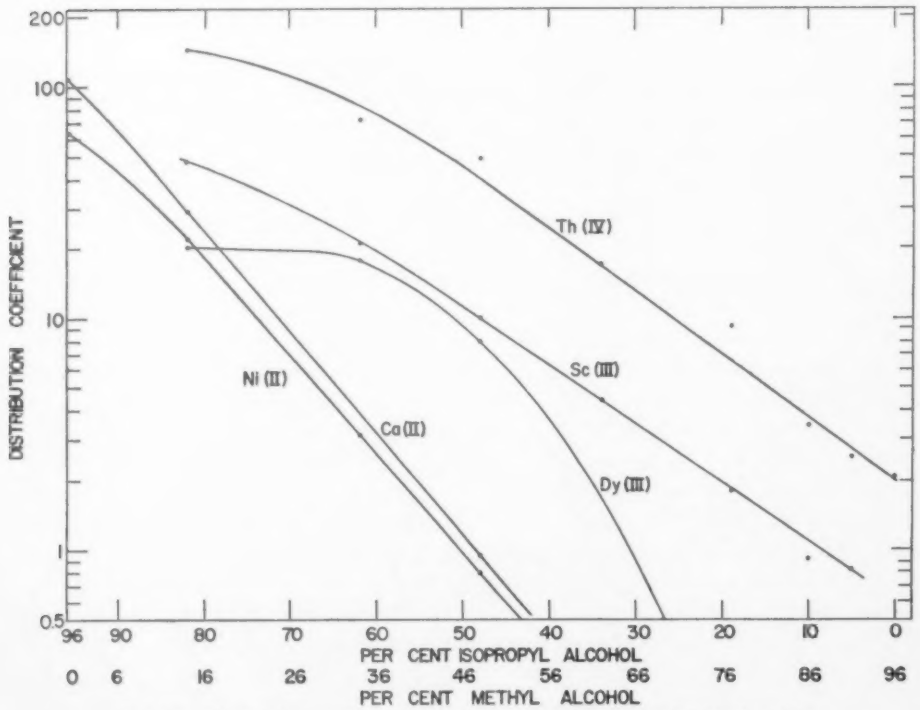

FIG. 14—Distribution coefficients of metal chlorides in 0·2*M* hydrochloric acid *vs.* concentration of methyl alcohol and isopropyl alcohol totalling 96%.

for the quantitative separation of several mixtures. It should be noted that a column of larger diameter was used for these separations than for those using 0·3*M* hydrochloric acid in ethyl alcohol (Table II). The larger column diameter allows greater loading and faster flow rates, but of course requires larger volumes of eluent for separation.

The distribution coefficient for thorium^{IV} is fairly high in 0·2*M* or 0·3*M* hydrochloric acid in 95% ethyl alcohol or isopropyl alcohol. Under these conditions the distribution coefficients of nickel^{II}, calcium^{II}, *etc.* are a little too high to permit a convenient separation from thorium^{IV}. However, Figs. 13 and 14 show that mixing

TABLE IV.—SEPARATION AND ANALYSIS OF SYNTHETIC METAL ION MIXTURES ON DOWEX 1 × 8, 200- TO 400-MESH, CHLORIDE-FORM RESIN. (5 × 2·2 CM.). QUANTITIES AND TYPE OF ELUTING AGENT ARE SIMILAR TO THOSE IN TABLE III.

Metal mixture	Taken, *mg*	Found, *mg*
Co^{II}-Cu^{II}		
Co	38·46	38·40
Cu	4·46	4·45
Ni^{II}-Co^{II}		
Ni	35·46	35·48
Co	4·82	4·82
Co^{II}-Fe^{III}		
Co	38·46	38·49
Fe	4·63	4·64
Mn^{II}-Co^{II}		
Mn	36·22	36·39
Co	4·82	4·83
Ca^{II}-Mn^{II}		
Ca	33·34	33·36
Mn	4·51	4·60
Ni^{II}-Mn^{II}		
Ni	35·46	35·55
Mn	4·51	4·65

methyl alcohol with isopropyl alcohol or ethyl alcohol provides a way to lower gradually the distribution coefficients of metal ions. In 0·2*M* hydrochloric acid-48% ethyl alcohol-48% methyl alcohol, a quantitative column separation of thorium^{IV} and nickel^{II} is obtained, although some tailing is observed in elution of the nickel. It appears that the use of mixed alcohols may also permit a fair separation of a nickel-dysprosium-thorium mixture.

In the mixtures analysed above, the sample constituents are present in approximately equal molar amounts. In Table IV, results are reported for the successful analysis of mixtures where two components are present in approximately a 10 to 1 ratio. So long as the column is not overloaded, a high ratio of one or more sample constituents to the others does not appear to cause any difficulty.

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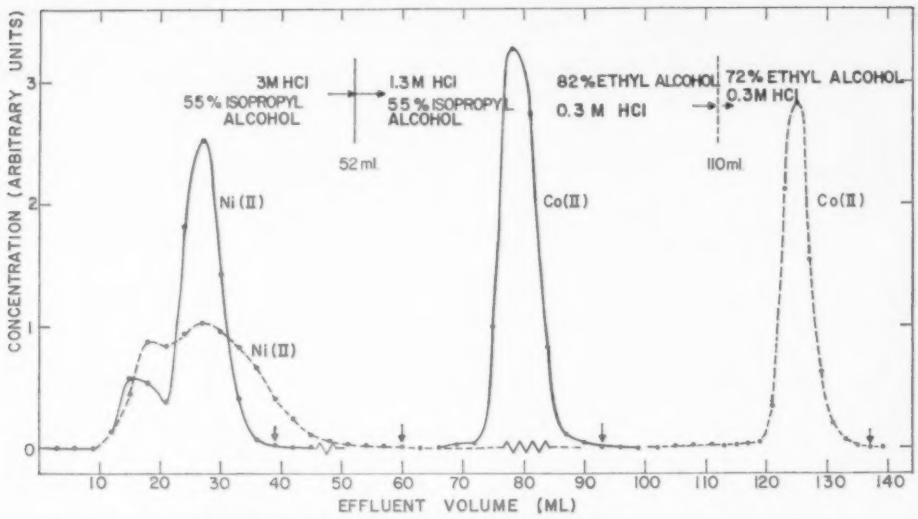

FIG. 15—Elution curves of a Ni^{II}-Co^{II} separation. Solid line represents elution by the varying hydrochloric acid-55% isopropyl alcohol eluting scheme. Dotted line represents elution by the varying percent of ethyl alcohol-0·3*M* hydrochloric acid eluting scheme. Flow rate of 1/4 to 1/3 ml/min and column dimensions of 5 × 2·2 cm (↓ = last detectable trace of metal ion.)

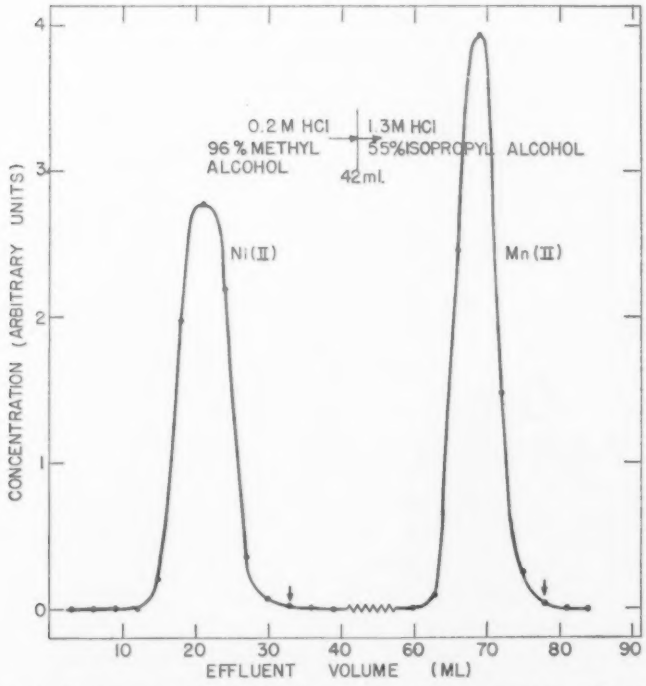

FIG. 16—Elution curve of a Ni^{II}-Mn^{II} separation. Flow rate of 1/4 to 1/3 ml/min and column dimensions of 6 × 2·2 cm. (↓ = last detectable trace of metal ion.)

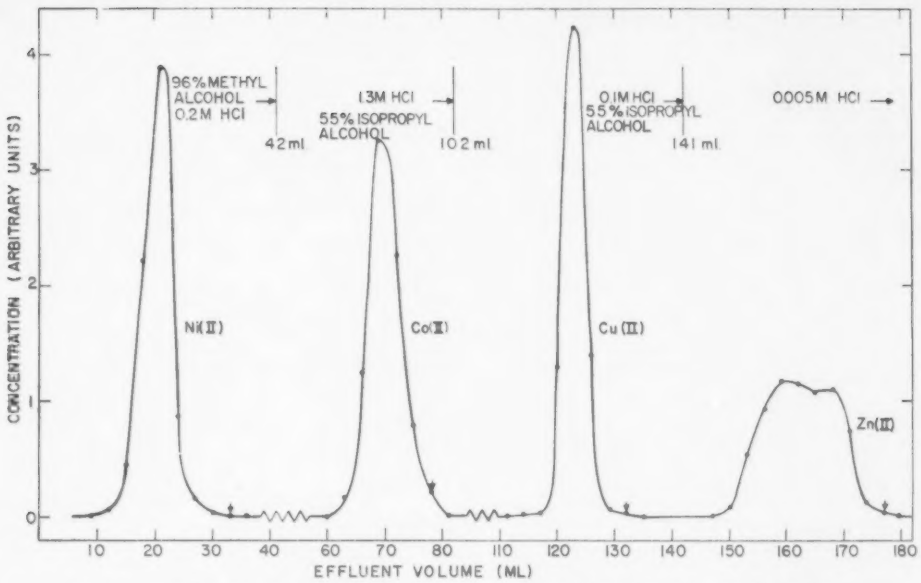

FIG. 17—Elution curve of a Ni^{II}-Co^{II}-Cu^{II}-Zn^{II} separation. Flow rate of 1/4 to 1/3 ml/min and column dimensions of 6 × 2·2 cm. (↓ = last detectable trace of metal ion.)

Zusammenfassung—Die Verteilungskoeffizienten für Metallionen zwischen einem Anionenaustauscher und einer flüssigen Phase (bestehend aus einer Mischung von Wasser und organischem Solvent), die Salzsäure enthält, wurden gemessen. Die Gegenwart von Salzsäure bewirkt, dass die Metallionen bei geringerer Säurekonzentration adsorbiert werden. In vielen Fällen sind die Verteilungskoeffizienten erheblich grösser als in Systemen mit wässriger Salzsäure. Bei sonst gleichen Bedingungen ist die Reihenfolge der Koeffizienten in Alkohol-Wasser-Salzsäure wie folgt: Isopropanol > Äthyl- > Methylalkohol. Säulentrennung von Metallionenmischungen können durchgeführt werden mittels Elution durch Alkohol-Wasser-Salzsäure-Mischungen verschiedener Zusammensetzung. Erfolgreiche Trennung einiger Gemische wird mitgeteilt.

Résumé—Les auteurs ont mesuré des coefficients de partage d'ions métalliques entre une résine échangeuse d'anions et des mélanges eau-solvant organique contenant de l'acide chlorhydrique. La présence d'un solvant organique provoque la fixation des ions métalliques à des concentrations d'acide chlorhydrique plus faibles. Dans de nombreux cas, les coefficients de partage sont beaucoup plus élevés que dans les systèmes eau-acide chlorhydrique. Les autres conditions étant comparables, l'ordre des coefficients de partage dans les mélanges alcool-eau-acide chlorhydrique est le suivant: alcool isopropylique, alcool éthylique, alcool méthylique. Les séparations sur colonne de mélanges d'ions métalliques peuvent être réalisées par élution avec des mélanges alcool-eau-acide chlorhydrique de différentes compositions. Des séparations d'un certain nombre de mélanges réalisées avec succès sont mentionnées.

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Talanta, 1961, Vol. 8, pp. 163 to 165. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

The determination of iron with 1,10-phenanthroline

(*Received* 22 *August* 1960. *Accepted* 24 *September* 1960)

A COMPREHENSIVE study of the use 1,10-phenanthroline for the spectrophotometric determination of iron and the effect of interferences has been made by Fortune and Mellon.[1] However, the effect of interfering ions was presented from the standpoint of the optimum pH to be used when certain elements are present. To determine iron by the 1,10-phenanthroline method, it is desirable to know the effect of various ions at one particular pH. We have studied the extent of interference, if any, of 68 elements on the determination of 100 μg of iron, at pH 4·0. This particular pH was chosen because it seemed to be the optimum when the effects of all of the elements were considered.

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EXPERIMENTAL

Procedure

To a 150-ml beaker were added a solution containing 10 mg of the element to be investigated, the standard iron solution (containing 100 μg of iron), 20 ml of 1*M* hydrochloric acid, 5 ml of 40% sodium acetate, and 2 ml of 10% hydroxylamine hydrochloride. The pH was adjusted to 4·0 $\pm$ 0·1 with a solution of sodium hydroxide and the solution was transferred to a 100-ml volumetric flask. Fifteen ml of 0·2% 1,10-phenanthroline were added and the solution was diluted to the mark. After 1 hr, the absorbance was measured at 510 mμ on a Cary Model 14 Recording Spectrophotometer, using 5-cm cells, with water as a reference. Samples containing precipitates were centrifuged before measuring. A number of elements precipitated either after the pH adjustment, or after the addition of 1,10-phenanthroline. The addition of citric acid before pH adjustment prevented precipitation in many instances and caused no interference, contrary to a published report.[2]

RESULTS

Elements which do not precipitate and do not interfere in the absence of citric acid

Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Zn, B, Al, Ga, In, Sc, Y, La, Si, Ge, Hf, As^{III}, V, Nb, Ta, F, Br, I, Mn^{II}, Mn^{VII}, Re, Pt, Ce^{IV}, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U^{VI}, P(as PO_4^{3-}; solutions containing P in 10-mg amounts must be allowed to stand overnight for complete colour development).

Elements which do not precipitate and do not interfere in the presence of 1 *g of citric acid*

Tl, Pb, Ti, Sb^{III}, Te, Bi, Sn, Zr, Mo, and W.

Elements which precipitate but do not interfere in the absence of citric acid

Au, Ba, Cd, Se, Ir (these elements also precipitated in the presence of citric acid) and Zr.

Elements which precipitate but do not interfere in the presence of 1 *g of citric acid*

Hg, Ir, Cd (solutions containing Cd in 10-mg amounts must be allowed to stand overnight for complete colour development).

Interfering elements

The following elements interfered, in 10-mg amounts, even in the presence of 1 g of citric acid. The percentage error in the determination of 100 μg of iron is indicated in parentheses. Cu(−100),

Sn(−53), Cr^{III} (+15), Cr^{VI} (+15), Co (−37), Ni (−100), Rh (+22), Pd (+7). None of these elements interfered when present in 1-mg amounts. When 15 ml of 0·3% 1,10-phenanthroline were used, no interference was noted with 10 mg of Cu or Sn.

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Summary—The extent of interference of 68 elements in 10-mg amounts in the spectrophotometric determination of iron with 1,10-phenanthroline, was studied at pH 4. Using the procedure described, which uses 1 g of citric acid and 15 ml of 0·3% 1,10-phenanthroline, and allowing the coloured solutions to stand overnight before the absorbance is measured, only Cr^{III}, Cr^{VI}, Co, Ni, Rh and Pd interfere. None of the elements studied interferes in 1-mg amount.

Zusammenfassung—Das Ausmass der Störungen von 68 Elementen (anwesend in 10 mg Mengen) bei der Bestimmung von Eisen mit 1,10 Phenanthrolin bei pH 4 wurde studiert. Folgende Methode wurde verwendet: Die Farbe wird in einer Lösung entwickelt, die 1 g Citroenensäure und 15 ml 0·3% ige Reagenslösung enthält, wobei über Nacht stehen gelassen wird. Unter diesen Bedingungen stören lediglich: Cr(III), Cr(VI), Co, Ni, Rh und Pd. Keines der studierten Elemente stört, wenn nicht mehr als 1 mg anwesend ist.

Résumé—Les auteurs ont étudié à pH 4 l'importance de l'interférence causée par 68 éléments en quantité de 10 mg dans le dosage du fer par la 1,10-phénanthroline. En employant le procédé décrit qui utilise 1 g d'acide citrique, 15 ml de 1,10-phénanthroline à 0,3 pour cent, et en laissant reposer pendant une nuit les solutions colorées avant de mesurer l'absorption, seuls Cr (III), Cr (VI), Co, Ni, Rh et Pd gênent. Aucun des éléments étudies né gêne pour des quantités de 1 mg.

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Effect of nitric acid on the extraction of iron with tri-n-octylphosphine oxide

(*Received* 26 *August* 1960. *Accepted* 10 *October* 1960)

Recently, we published a method for the determination of iron in beryllium and beryllium oxide.[1] Because few elements interfere with the determination, we have applied the method to many different materials with considerable success. However, solutions which contain nitric acid from the dissolution of samples must be treated before the extraction of iron with tri-n-octylphosphine oxide (TOPO) in order to eliminate the deleterious effect of the nitrate ion.

With one exception no information is available concerning the effect of nitric acid on the extraction of iron with TOPO. White[2] states that iron is not extracted from 1*M* or 7*M* nitric acid. When it was found that the presence of nitric acid caused low results, the question arose: were the low results due to incomplete extraction of iron, or to the destruction by nitric acid of the colour-forming reagent, 1,10-phenanthroline? It has been established that nitric acid prevents the complete extraction of iron from a chloride medium with TOPO. This was established in the following manner. One ml of 15*M* nitric acid was added to 35 ml of 7*M* hydrochloric acid containing 100 μg of iron. This solution was extracted with 0·01*M* TOPO in the usual manner. The aqueous phase was treated with a few drops of sulphuric acid, evaporated to dryness, and the iron determined by the aqueous 1,10-phenanthroline procedure; 45 to 50% of the iron originally added was found. The organic phase was treated

with 3*M* sulphuric acid to remove the iron, and the acid solution evaporated to fumes of sulphuric acid to remove any nitrate. The acid solution was treated with hydrochloric acid and the iron extracted with TOPO and determined in the manner previously described;[1] 45 to 40% of the iron was found. The 90 to 95% recovery of iron is within expected experimental error. The results are adequate to prove that nitric acid interferes with the extraction of iron from a chloride medium by TOPO.

It should be pointed out that in White's report[2] it is stated that extraction of iron is 90% complete from 7*M* HCl containing 1*M* HNO_3. This lends additional experimental support to these conclusions.

J. O. Hibbits
W. F. Davis
M. R. Menke

Aircraft Nuclear Propulsion Department
General Electric Company
Cincinnati 15, *Ohio, U.S.A.*

Summary—Nitric acid prevents the complete extraction of iron from a chloride medium with tri-n-octylphosphine oxide (TOPO).

Zusammenfassung—Es wurde gefunden, dass Salpetersäure die vollständige Extraktion von Eisen aus einem chloridhaltigen Medium mit Tri-n-octylphosphinoxyd stört.

Résumé—L'acide nitrique empêche l'extraction complète du fer par l'oxyde de tri-n-oxtylphosphine (TOPO) en milieu chlorure.

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REFERENCES

[1] J. O. Hibbits, W. F. Davis and M. R. Menke, *Talanta*, 1960, **4**, 61.
[2] J. C. White, AEC-Project Report ORNL-2382, 1957.

Talanta, 1961, Vol. 8, p. 166. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

RE: *J. Inorg. Nucl. Chem.*, 1959, **9**, 252; 1960, **11**, 124; 1960, **13**, 261, 269: *Talanta*, 1960, **3**, 219.

Sir:

I wish to acknowledge the contribution which Emeritus Professor H. T. S. Britton made to the above studies. The work was done in his former Department of Chemistry at University College, Exeter (now the University of Exeter). The programme was suggested by him and done under his direction and supervision, as required by the London University Ph.D. regulations for External Students.

I should like to record my gratitude to him for his guidance and criticism in this work, which is of course in his long-standing area of interest, and to express regrets for the previous omission of his name from these papers.

PETER CANNON

Alplaus, N.Y., U.S.A.
December 6, 1960

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BOOK REVIEWS

Advances in Inorganic Chemistry and Radiochemistry, Vol. 2. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press Inc., New York, 1960. Pp. viii + 392.

THIS volume, like the first, is an indispensable work of reference for research workers and teachers of inorganic chemistry. It comprises eight chapters, by contributors of world standing.

Much of the book is devoted to the covalent chemistry of sulphur, which has undergone remarkable developments in the last ten years. The chapter by O. Foss on "Structures of Sulfur Chain Compounds" and that by M. Becke-Goehring on "Amides and Imides of the Oxyacids of Sulphur" deal largely with one of the two main directions of advance, namely that concerned with the synthesis, structure and transformations of chain and ring sulphur compounds. Another rapidly expanding field, that of $-SF_5$ derivatives, is covered in G. H. Cady's "Fluorine-containing Compounds of Sulphur."

J. D. Dunitz and L. E. Orgel contribute a chapter on "The Stereochemistry of Ionic Solids" in which the impact of the ligand field theory on classical conceptions of ionic crystal structures is discussed fully and with exceptional clarity. F. G. A. Stone's "Chemical Reactivity of the Boron Hydrides" and J. J. Katz and I. Sheft's "Halides of the Actinide Elements" are both valuable contributions of unusual character. J. Eisch and H. Gilman's "Organometallic Compounds" is a survey of recent advances in methods of operation in this field of chemistry, and of new principles and generalisations which have lately emerged. The only article on nuclear chemistry is "Mass Spectrometry in Nuclear Chemistry" by H. G. Thode, C. C. McMullen and K. Fritze. It embodies the results of more than a decade of patient and unobtrusive work without which our present understanding of nuclear reactions could not have been acquired.

All the chapters cover the literature through 1958, in some cases into 1959, except "Fluorine-containing Compounds of Sulphur" which is only complete through 1956. Unfortunately, therefore, the recent spectacular developments in sulphur tetrafluoride chemistry are not mentioned at all.

H. G. HEAL

X-Ray Powder Photography in Inorganic Chemistry, R. W. M. D'EYE and E. WAIT. Butterworths Scientific Publications, London, 1960. Pp. viii + 222. 45s.

THIS book has been written to provide the research chemist, having no experience of crystallography, with the essential information to enable him to use the powder technique to the best advantage in his work.

Chapters are included on the production and isolation of the necessary monochromatic X-ray beam, on the design and calibration of the Debye-Scherrer camera and the several focusing types of camera, and on sample preparation. Much useful practical advice is given and the techniques available are compared as to suitability for various applications.

The usual aim of the powder technique is to characterise the crystal system of the compound examined and determine the lattice parameters accurately. The authors give a comprehensive survey of the graphical and analytical methods available for extracting this information from a powder pattern. Many worked examples make these two chapters a most valuable part of the book.

A chapter on crystallographic theory discusses the properties of two and three dimensional lattices and relates these to the symmetry found in crystals. The various symmetry elements are explained and their combination into a space group to describe a particular crystal symmetry is discussed.

A detailed treatment of the factors affecting the intensity of a diffraction line is given. This is followed by a section on determination of atomic positions in the unit cell. Three examples, of a highly symmetrical structure with positions fixed by symmetry and of less symmetrical structures with one or more parameter variable, are used to discuss this topic in a most useful and practical way.

A long chapter on applications concludes the book. Some topics dealt with are qualitative and quantitative analysis, determination of chemical formulae, study of semiconductors, anomalous mixed crystals, solid-solid reactions. A good index makes it easy to refer to any specific topic and adequate and up-to-date references are collected at the end of each chapter.

The book should prove a valuable addition to the library of any crystallographer, chemist or physicist. It is written in a practical way, the style is concise but nowhere is accuracy sacrificed to brevity. The treatment is fresh and should stimulate the interest of readers in the technique. The authors have obviously put into the book the results of their own experience as chemist-crystallographers. They have succeeded in writing a book self-evidently founded on a thorough acquaintance with their subjects.

B. J. MCDONALD

Advances in Fluorine Chemistry, I. Edited by M. STACEY, J. TATLOW and A. G. SHARPE. London. Butterworth's Scientific Publications, 1960. 45s.

UNTIL the present book came out, Volume I of the "Mellor" supplement, now nearly five years old, contained the most recent comprehensive general account of fluorine chemistry. Five years are a long time in the history of this element, and the need for a good new textbook has been getting more and more pressing. Since the task of writing up fluorine adequately is now almost beyond the capacity of any one person or small group, it has been decided to publish a continuing series of collective volumes, of which this is the first. It is planned to cover both fundamental and industrial developments. Fluorocarbon chemistry alone, potentially as large as the field of organic chemistry itself, could ensure an adequate supply of material for many future volumes.

All the contributors to Volume I are experts of international reputation. The book is throughout interesting, topical, up-to-date and fully documented. The following subjects are dealt with: halogen fluorides: transition metal fluorides and their complexes; fluoroboric acids and their derivatives; electrochemical fluorination; and fluorination with high-valency metallic fluorides.

This is a very useful and reasonably priced book.

H. G. HEAL

Elementary Titrimetric Analysis. A. M. G. MACDONALD. Butterworth, London, 1960. pp. viii + 133. 12s. 6d.

THIS little book is a well-balanced presentation of titrimetric methods for school and technical college students beginning their serious study of quantitative analysis.

Short introductory chapters deal competently with nomenclature and with the use and maintenance of apparatus. Sections on acid-base titrations, argentimetric methods, redox titrations and complexometric titrations are each based on a sound discussion of principles and the procedures are indicated in a nicely-varied selection of exercises. The theory of redox titrations, in particular, is admirably expounded in relation to the use of permanganate, dichromate, ceric sulphate, mercurous nitrate and iodimetric methods.

In a book which attempts so much within its 123 pages of text, it is perhaps inevitable that the treatment is sometimes rather dogmatically concise. Fuller descriptions of some of the procedures and more detailed guidance on the recording of results are desirable at this level. Many teachers, mindful of the pitfalls of a rule-of-thumb approach to titrimetric calculations, will not share the author's enthusiasm for $v_1n_1 = v_2n_2$ and would welcome more attention to exercises which aim at facility in the manipulation of gram-equivalents. There are a few inconsistencies, as when the author

stresses the value of a high equivalent weight in a standard substance, yet occasionally specifies quantities which are unrealistically small for elementary work; and when her description of the neutralisation curve of phosphoric acid goes beyond what can be seen in her diagram. But these are minor blemishes in an excellent book. The student who uses it will proceed with confidence to any of the standard works mentioned in the short bibliography.

The book is well printed and strongly bound. A few additional pages in a subsequent edition would enable the author to improve the exposition in places and thereby increase the usefulness of the book to students.

J. McG. Jackson

The Routine Analysis of Copper Base Alloys. Frank J. Versagi. Chemical Publishing Co. Inc., New York, 1960. pp. 168 $5.00.

This slim volume is a collection of methods of analysis likely to prove useful to those for whom the author states it is intended. Even though "theroretical" chemistry has been deliberately excluded as far as possible, it is disquieting to find to be inaccurate some of the little there is. For example on p. 70 we are told that aluminium precipitates from a solution made alkaline with 10 ml of saturated caustic soda solution, and on p. 71 that "boiling with sodium hydroxide drives off the nitric acid." The statement on p. 15 that for routine work it is never necessary to weigh beyond four significant figures is obviously nonsense when electrolytic methods are used as often as in copper alloy analysis. On the practical side, one may ask what is the purpose and effect of adding 1 drop of 0.1*N* hydrochloric acid to the electrolyte before determining copper (p. 30).

The book is not free from typographical errors, the worst being the misplacement of a whole line on p. 157, and the consistent use throughout of Mu for mμ. Although the book undoubtedly achieves its avowed aims, one wonders whether they are completely desirable ones or whether it would be better to follow Hillebrand in wishing to produce analytical chemists rather than chemical analysts. Finally, five dollars seems a lot to pay for 168 pages, 20 of which are completely blank, being unsullied even by the page numbers they should bear.

R. A. Chalmers

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TALANTA MEDAL

THE Editorial Board and Publishers of TALANTA take pleasure in announcing that with the approval of the Advisory Board they recommend the first award of the Talanta Medal to

PROFESSOR FRITZ FEIGL.

Through the kind co-operation of the organisers of the forthcoming Congress on Analytical Chemistry in Budapest on April 24–29, 1961, it is proposed that the award will be made to Professor Feigl at that meeting.

PROFESSOR FEIGL is famous for his "spot tests." These sensitive colour and precipitation reactions have been used to detect traces of various inorganic and organic materials. In itself this work is amongst the most notable contributions to analytical chemistry of the past two generations; but it is unfortunate that the fundamental ideas behind Feigl's work have, on the whole, been overlooked. In many cases Feigl has discovered these reactions himself, and this alone constitutes a chemical contribution of the first rank.

The colour reactions in turn have formed the basis for quantitative determinations by later workers, and in many cases the discoverer has been overlooked. The vast development of paper chromatography would have been seriously impeded had not Feigl's spot tests been available for detecting separated components. Feigl was probably the first to place the use of masking reactions on a scientific basis, and many of the reactions which he uses in his spot tests to overcome the effects of interfering ions have been adapted to use in many other analytical processes. Again he has received little credit for this.

These are just a few examples of the great impact that his work has had on modern analytical chemistry. He is undoubtedly one of the great living analytical chemists; his study of reactions has been a life-time's work; and probably no-one has contributed so many new reactions to the whole field of chemistry. His work has been going on continuously for nearly fifty years. His results have been applied in fields as far apart as qualitative testing, paper chromatography and spectrophotometry. It is felt that he is a most worthy recipient of the Medal.

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EDITORIAL NOTE

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THE present issue of TALANTA marks a stage in the Journal's development which, we feel, requires some comment.

In the first place, the Editor would like to thank all his subscribers and contributors for their patience during the teething troubles of a new Journal. Teething troubles are inevitable, but are not always sufficiently appreciated to be tolerated with indulgence. The fact that, in general, both contributors and subscribers have shown an understanding of the difficulties has been a kindness which has been more recognised by the Editor than acknowledged.

This issue, which is to some extent anomalous in being a double issue, should appear in the first week of March. From this point onwards, we hope that each issue will appear monthly in the month listed on the cover. This is a state of affairs which our subscribers and contributors will be only too well aware has not occurred in the past.

Qui s'excuse, it is said, *s'accuse:* but when the decision was taken, in September 1959, to change, in January 1960, from bimonthly to monthly appearance, both editorial and printing difficulties had to be overcome. In consequence, our publication dates during 1960 were, to say the least, erratic, and in general long overdue; although on this point we feel that our subscribers had more complaint than our contributors, since the actual time from acceptance to publication has not, on the whole, been unduly protracted.

As we emerged from the difficulties arising from the change in time-schedule, we became involved—very willingly, but to the detriment of our normal programme—in the production of the special issue in honour of Professor Willard, which has just appeared. This called for additional work, both on the editorial side and with the printer. The special Gatlinburg volume was a further strain on the printer, although editorial headaches were nominal, since our American colleagues made themselves responsible for these.

At this point it is only appropriate to acknowledge the co-operation that has been given throughout by our printers, whose patience we must frequently have strained almost (although fortunately never quite) to breaking point.

Rather belatedly, we would take this opportunity to explain the new system of volume numbers. Up to the present there have been three volumes per year, and since we commenced on a bimonthly basis in the middle of a year, this has resulted in non-coincidence of years with volume numbers. From January 1961, we propose to adhere to the more usual "one year, one volume" basis, so that the 1961 volume will be Volume 8, and will comprise twelve issues. Volume 7, which began with the November-December 1960 issue, has been completed by the special Willard issue (which in itself is rather larger than an average double issue). Volume 6 was the special Gatlinburg issue, and Volume 5 is made up by the July-October 1960 issues.

In conclusion, we would like to reiterate that from this issue forward we expect to publish in the first week of the appropriate month. It may be necessary, from time to time, to close matter for press with a reduced number of pages. But this will be offset by additional pages in other issues, so that the average number of pages per issue will remain as before.

In the near future we hope, in response to requests, to give some account of our editorial and refereeing policy. At the moment we would merely draw the attention of our readers to the recently revised Notes for Contributors, which we expect, on that occasion, to comment on at more length.

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NOTICES

The following meetings have been arranged

Friday 3 *March* 1961: **Society for Analytical Chemistry:** Annual General Meeting, 2.15 p.m., and Address of Retiring President, Mr. R. C. CHIRNSIDE, F.R.I.C. *The Enlargement of Horizons in Analytical Chemistry*. 2.45 p.m. Burlington House, London, W.1.

Biennial Dinner. Fishmonger's Hall, London Bridge, London, E.C.4. 7.15 p.m. for 7.45 p.m.

Wednesday 8 *March* 1961: **Society for Analytical Chemistry,** Midlands Section: *Some Newer Reagents in Analytical Chemistry:* Professor R. BELCHER, D.Sc., F.R.I.C. The Technical College, Luton. 6.30 p.m.

Friday 10 *March* 1961: **Society for Analytical Chemistry,** Western Section and **Royal Institute of Chemistry,** South Wales Section: Joint Meeting: *Vapour Phase Chromatography:* Mr. A. VERDIN. Swansea.

Tuesday 14 *March* 1961: **Society for Analytical Chemistry,** Midlands Section: Annual General Meeting. Regent House, Birmingham. 6.30 p.m.

Wednesday 22 *March* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Discussion Meeting. *The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 23 *March* 1961: **Society for Analytical Chemistry,** Midlands Section: *Measurement of pH and Electrode Potential for Analytical Purposes:* Dr. G. MATTOCK. The Technical College, Nottingham. 7.00 p.m.

Friday 24 *March* 1961: **Society for Analytical Chemistry,** Scottish Section: *Non-aqueous Titrimetry:* Mr. G. R. JAMIESON, B.Sc., A.R.I.C. and Dr. E. R. LANE, F.R.I.C. Glasgow.

Saturday 25 *March* 1961: **Society for Analytical Chemistry,** Physical Methods Group and North of England Section: Joint Meeting: *The Analysis of Intact Samples*. City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Wednesday 29 *March* 1961: **Society for Analytical Chemistry:** Demonstration Meeting of Laboratory-Built Equipment. Chelsea College of Science and Technology, Manresa Road, London, S.W.3.

Thursday 6 *April* 1961: **Society for Analytical Chemistry,** Biological Methods Group: Discussion Meeting: *Principles Involved in Collaborative Studies*: Mr. S. A. PRICE, B.Sc., F.R.I.C. *The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 12th *April* 1961: **Society for Analytical Chemistry** and **Oil and Colour Chemists Association:** Joint Meeting. Wellcome Building, Euston Road, London, N.W.1. 7.00 p.m.

Wednesday 26 *April* 1961: **Society for Analytical Chemistry,** Midlands Section and Physical Methods Group: Joint Meeting: *Spectrofluorimetry:* Dr. C. A. PARKER. *Tesla Luminescence:* Dr. R. J. MAGEE. University, Edgbaston, Birmingham, 15. 7.00 p.m. Preceded by a visit to the Mond Nickel Co. Ltd. 3.00 p.m.

Friday 28 *April* 1961: **Society for Analytical Chemistry,** Western Section and **Society for Chemical Industry,** South Wales Section and Food Group: Joint Meeting: *Modern Legislation in Relation to Food Additives:* Mr. C. A. ADAMS, C.B.E., B.Sc., F.R.I.C. Cardiff.

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Friday 28 *April* 1961: **Society for Analytical Chemistry,** North of England Section and Scottish Section: Joint Meeting: *Ion Exchange:* Dr. T. R. E. KRESSMAN, F.R.I.C. *The Determination of Nitrates with Particular Emphasis on the Use of Dead-stop Titrimetry:* Mr. A. F. WILLIAMS, B.Sc., F.R.I.C. Central Hotel, Victoria Viaduct, Carlisle. 7.15 p.m.

(*Monday–Tuesday* 8–9 *May* 1961: Analytical Chemistry Subject Division and the Cornwall Ontario) District Section of the **Chemical Institute of Canada:** *Symposium on Titrimetric Methods of Analysis.* Parkway Hotel, Cornwall, Ontario.

The symposium will consist of three half-day sessions, each of which will be devoted to one of the following subjects: *Complexometric Titrations, Titrations in Non-aqueous Media* and *Electrometric Titrations.* Professor J. S. FRITZ, Professor G. N. REILLY and Dr. G. BUC will be delivering lectures covering these three aspects of titrimetric analysis.

Enquiries should be addressed to Mr. J. R. MCCALLUM, Courtaulds (Canada) Ltd., Cornwall, Ontario.

Tuesday–Saturday 19–23 *September* 1961: Analytical Commission of the Chemical Committee of the **Polish Academy of Sciences** with the collaboration of the **Polish Chemical Society** and the **Institute of Nuclear Research:** *Third Polish Conference on Emission Spectral Analysis.* Jelitkowo near Gnańsk.

The conference will be devoted to theoretical and experimental works performed recently in the field of emission spectral analysis, and its application to research and industry.

The general programme is as follows:

1. *General problems: apparatus, excitation sources, interpretation of results, etc.*
2. *Spectral analysis of metals.*
3. *Spectral analysis of non-conducting samples.*
4. *Spectral analysis of solutions, including flame photometry.*
5. *X-ray emission and X-ray fluorescence analysis.*

Lectures will be held in Polish, English, Russian or German, and all papers will be published in a special edition of *Chemia Analityczna.*

Enquiries should be addressed to Mgr. ADAM HULANICKI, Komisja Analityczna, Komitsetu Nauk Chemicznych PAN, Warsawa 22, Pasteura I, Poland.

B.S.I. News announces the following new British Standards:

B.S. 3279: *Seedlac:* 1960. This supersedes the relevant parts of B.S. 954, 'Lac'. Provision is made for six grades which correspond approximately to six grades in ISO/R 55 'Seedlac' and which differ in matter insoluble in hot alcohol, non-volatile matter soluble in cold alcohol and colour index. The scope, description, sample, volatile matter, matter insoluble in hot alcohol and method of expressing the analytical results are specified. Optional clauses, covering the requirements of different users, are for colour index, matter soluble in water, non-volatile matter soluble in cold alcohol and wax. (Price 5s.)

B.S. 3280: *Hand-made shellac:* 1960. This supersedes the relevant parts of B.S. 954, 'Lac'. Provision is made for five grades which correspond approximately to the top five out of six grades in ISO/R 55 'Shellac' and which differ in matter insoluble in hot alcohol, non-volatile matter soluble in cold alcohol, colour index and ash. The scope, appearance and colour, sample, matter insoluble in hot alcohol, orpiment, rosin and method of expressing the analytical results are specified. Optional clauses, covering the requirements of different users, are for colour index, volatile matter, matter soluble in water, non-volatile matter soluble in cold alcohol, ash, grit wax, flow, life under heat, acid value, iodine value, arsenic and lead. (Price 10s.)

The following Amendment Slip is also announced:

B.S. 1728: *Methods for the analysis of aluminium and aluminium alloys: Part* 2 1952: *Determination of magnesium.* Amendment No. 2: PD 3886. (Gratis)

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PAPERS RECEIVED

Selection of complexing agents for complexometric titrations: ERKKI WÄNNINEN. (21 *November* 1960).

Determination of water by near infrared spectroscopy: D. A. KEYWORTH. (21 *November* 1960).

Metallochromic indicators—X: A new mixed indicator for the chelatometric determination of calcium: V. SVOBODA, V. CHROMÝ, J. KÖRBL and L. DORAZIL. (23 *November* 1960).

Thermogravimetric decomposition of thorium 8-hydroxyquinolate: C. E. CROUTHAMEL and C. E. JOHNSON. (28 *November* 1960).

Spectrophotometric determination of palladium with nitrilo-acetic acid: P. G. DESIDERI and F. PANTANI. (29 *November* 1960).

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The anion-exchange separation of technetium, rhenium and manganese: MIROSLAV PIRS and ROBERT J. MAGEE. (30 *November* 1960).

Potentiometrische Titrationen—I: Allgemeine Betrachtungen und die Theorie chelatometrischer Titrationen ohne Anwendung eines Indicators: H. FLASCHKA. (7 *December* 1960).

Murexide (ammonium purpurate) as an indicator in thorium-ethylenediaminetetra-acetic acid titrations: SATANDRA PRASHAD SANGAL and ARUN K. DEY. (12 *December* 1960).

Mitteilung über quantitative organische Analyse—XXVIII: Eine automatische Methode zur Mikrobestimmung von Kohlenstoff, Wasserstoff und Stickstoff: M. VECERA. (14 *December* 1960).

Applications de la chélatometrie—VII: Dosage volumétrique des *o*-acyl-phènols. CLAUDE HENNART et (Mme.) YVETTE LEFEVRE. (15 *December* 1960).

Spectrophotometric study of the complex of lanthanum and Alizarin Red S: TOSHI KAWASHIMA, HARUNO OGAWA and HIROSHI HAMAGUCHI. (19 *December* 1960).

Spectrophotometric determination of thorium in low-grade minerals and ores: ANNA-LISA ARNFELT and INGA EDMUNDSSON. (19 *December* 1960).

New colour reactions of elemental sulphur and carbon disulphide: T. URBÁNSKI. (19 *December* 1960).

Use of "tagged" atoms for the investigation of precipitate exchange reactions: L. ERDEY, D. HEGEDUS and I. PORUBSZKY. (2 *January* 1961).

Organic analysis—XXIX: A new spraying reagent for reducing sugars on paper chromatograms: TSUTOMU MOMOSE and MASARU NAKAMURA. (2 *January* 1961).

Fluorometric determination of zirconium with quercetin: Separation of interference by extraction with TTA: DAVID M. HERCULES. (3 *January* 1961).

Determination of fluorine in mineral waters using Xylenol Orange: ROMAN VALACH. (4 *January* 1961).

Salting-out chromatography—VII: Analysis of mixtures of dialkylphosphoric acids, alkane phosphonic acids and orthophosphoric acid: F. JAKOB, K. C. PARK, J. CIRIC and WM. RIEMAN III. (6 *January* 1961).

Titrimetric determination of vanadium^{III} with sodium metavanadate using oxidation-reduction indicators: B. V. S. R. MURTHY snd G. GOPALA RAO. (9 *January* 1961).

The latent heat of fusion of ethylene carbonate: R. F. KEMPA and W. H. LEE. (10 *January* 1961).

The spectrophotometric determination of the ionisation constants of some derivatives of barbituric acid: MURRAY E. TAYLOR and REX J. ROBINSON. (10 *January* 1961).

Applications de la chélatométrie—IX: Semi-microdosage de l'iode dans les substances organiques en présence des autres halogènes: CLAUDE HENNART. (13 *January* 1961).

Extraction of arsenic^{V} from H_2SO_4-KBr solutions and its analytical use: K. ŠTUDLAR. (16 *January* 1961).

Colour reactions of some 1,4-dihydroxyanthraquinones with aluminium and beryllium: E. GUY OWENS II and JOHN H. YOE. (16 *January* 1961).

Homogeneous precipitation from mixed solvents: LESTER C. HOWICK and JERRY L. JONES. (16 *January* 1961).

The determination of thiomalic acid: A. I. BUSEV and SHAN FAN. (17 *January* 1961).

The consecutive radiometric titration of several elements using the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline containing sulphur-35: A. I. BUSEV and V. M. BYRKO. (17 *January* 1961).

Contributions to the basic problems of complexometry—V: Mutual masking of iron and manganese: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (19 *January* 1961).

Isotopic dilution analysis by solvent extraction—III: Highly selective determination of trace amounts of mercury: JAROMÍR RŮŽIČKA and JIŘÍ STARY. (19 *January* 1961).

Titrimetric determination of titanium^{III} with sodium metavanadate—I: Use of neutral red, phenosafranine or safranine-T as oxidation-reduction indicators: B. V. S. R. MURTHY and G. GOPALA RAO. (23 *January* 1961).

Potentiometric titration of titanium^{III} with vanadium^{IV}: B. S. V. R. MURTHY and G. GOPALA RAO. (23 *January* 1961).

Titrimetric determination of indigo sulphonate with potassium iodate: G. GOPALA RAO and N. VENKATESWARA RAO. (23 *January* 1961).

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STUDY OF THE REDUCTION WAVES OF THE ISOMERS OF NITROPHENOL BY MEANS OF THE ALTERNATING CURRENT POLAROGRAPH

TAKEO TAKAHASHI and HIDEKO SHIRAI
Institute of Industrial Science, University of Tokyo, Japan

(*Received* 2 *May* 1960: *Accepted* 30 *October* 1960)

Summary—In a study of the a.c. polarography of *o*-, *m*- and *p*-nitrophenols it was found that the wave heights were proportional to the concentrations of nitrophenols in potassium hydroxide and ammonium chloride-ammonium hydroxide base solutions. The reduction waves for d.c. polarograms in certain base solutions were not solely diffusion-controlled. This applied to the first wave of *p*-nitrophenol in 0·2*M* or stronger potassium hydroxide and in sodium carbonate solutions, and similarly to *m*-nitrophenol in 0·5*M* to 0·8*M* potassium hydroxide solutions and *o*-nitrophenol in solutions in the pH range 4–7. Because the a.c. polarograms are purely diffusion-controlled such polarography is preferred to d.c. polarography for the determination of nitrophenol isomers.

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INTRODUCTION

THE reduction waves of the three isomers of nitrophenol (*o*-, *m*- and *p*-nitrophenol) have been studied extensively by means of the direct current polarograph. The values of the half-wave potentials in many supporting electrolytes of various pH values have been measured and the existence of two reduction waves due to the undissociated and dissociated nitrophenol was established by Shikata and Watanabe.[1] Astle and McConnel[2] and Oeshpande and Parthasarathy[3] discussed the difference between the polarographic behaviour of *p*- and *o*-nitrophenols in acidic solution. They concluded that through hydrogen bonding *o*-nitrophenol forms intermolecular compounds which are stable during the polarographic reduction in acidic solution.

In the present paper, the authors describe the a.c. polarographic behaviour of nitrophenol isomers, keeping in mind its possible application to chemical analysis.

Since the a.c. polarograms of *o*-, *m*- and *p*-nitrophenols showed higher wave heights in alkaline solution than in acidic solution, mainly alkaline base solutions were employed for this work.

The a.c. polarograms of nitrophenol isomers in alkaline solutions were found to be solely diffusion-controlled.

EXPERIMENTAL

Apparatus

The self-recording d.c. and a.c. polarographs used were constructed in our laboratory; details have already been reported.[4] In the present experiments, except in a few cases, addition of gelatine to the supporting electrolytes was not made. An agar-agar bridge was used for the connection between sample solution and calomel electrode.

Hydrogen gas was employed for the removal of the dissolved oxygen. The a.c. voltage superimposed on the d.c. voltage was 10 mV and the other conditions were as follows:
Capacity of the standard condenser (Cs) = 0·2 μF.
Standard resistance (Rs) = 0·5 KΩ.
Mercury drop rate (m) = 2·79 mg/sec.
Mercury drop time (t) = 4 sec (in 1*N* KOH solution and at −1·0 V).

RESULTS

(1) *p-Nitrophenol*

(i) A.c. and d.c. polarograms in sodium carbonate and sodium phosphate solutions: Fig. 1 shows the a.c. (a) and d.c. (d) polarograms of *p*-nitrophenol in 0·25*M* sodium carbonate solution. These polarograms indicate the existence of two reduction waves.

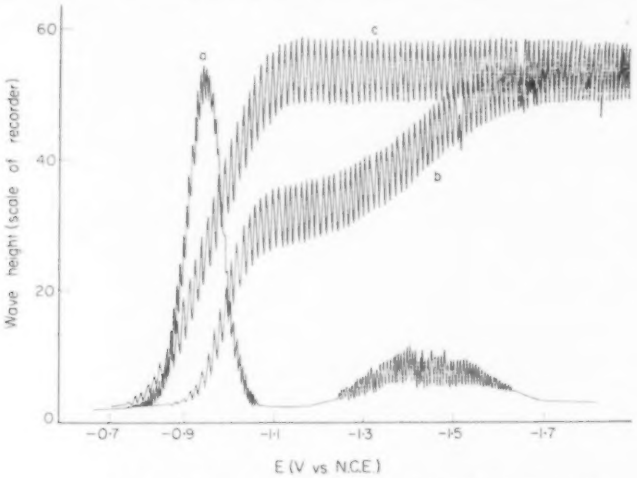

FIG. 1.—d.c. and a.c. polarograms of 1m*M* *p*-nitrophenol
(a) a.c. polarogram in 0·25*M* sodium carbonate solution
(scale, 20 = 0·4 mV)
(b) d.c. polarogram in 0·25*M* sodium carbonate solution with 0·001 % gelatine
(scale, 20 = 12 μA)
(c) d.c. polarogram in 1·8 % sodium borate solution with 0·001 % gelatine
(scale, 20 = 12 μA)
Temp. 25°

The first wave has its peak potential at −0·94 V v. NCE and the second wave that at −1·42 V v. NCE in the a.c. polarogram. In the d.c. polarogram (with 0·001 % gelatine) the half-wave potential of the first wave is at −0·99 V v. NCE and its total wave height is almost equal to that of the single wave height of the d.c. polarogram (c) in 1·8 % sodium borate solution (pH 9·8) with 0·001 % gelatine. Table I shows the

TABLE I.—RELATIONSHIP BETWEEN THE FIRST "WAVE HEIGHTS" IN D.C. AND A.C. POLAROGRAMS AND THE CONCENTRATION OF SODIUM CARBONATE

Concentration of Na_2CO_3, *M*		0·5	0·25	0·1
The first "wave height"	d.c., μA	19·8	17·4	15·6
	a.c., mV	1·04	1·02	1·00

relationship between the first "wave heights" in d.c. and a.c. polarograms and the concentration of sodium carbonate.

According to Table I, the first "wave height" of the d.c. polarogram increases with the concentration of the supporting electrolyte, but that of the a.c. polarogram remains almost constant. Similar results were found in the case of 0·35*M* sodium phosphate

TABLE II.—RELATIONSHIP BETWEEN THE "WAVE HEIGHTS" OF A.C. AND D.C. POLAROGRAMS AND pH IN SODIUM PHOSPHATE SOLUTION

pH	12·8	12·6	12·3	12·0	11·5
The first "wave height" a.c., mV	1·04	1·04	0·99	0·97	0·88
d.c., μA	15·0	15·0	15·2	17·8	21·0

solution. However, Table II shows the "wave heights" obtained for a.c. and d.c. polarograms using sodium phosphate solution of different pH values.

In the above experiment the pH value was changed by addition of disodium orthophosphate to trisodium orthophosphate, but the total concentration of phosphate was held constant (0·35*M*). As shown in Table II, the height of the first wave of the a.c. polarogram increases with pH, but that of the d.c. polarogram decreases.

Fig. 2 shows the relationship between the height of the first wave of the d.c. polarogram of *p*-nitrophenol in 0·50*M* sodium carbonate solution and $\sqrt{h}$. The line (a) does not pass through the origin. The control line (b) which refers to the "wave height" of 1m*M* lead nitrate in 0·2*N* potassium hydroxide solution, passes through the origin. It is considered that the first waves of d.c. polarograms of *p*-nitrophenol

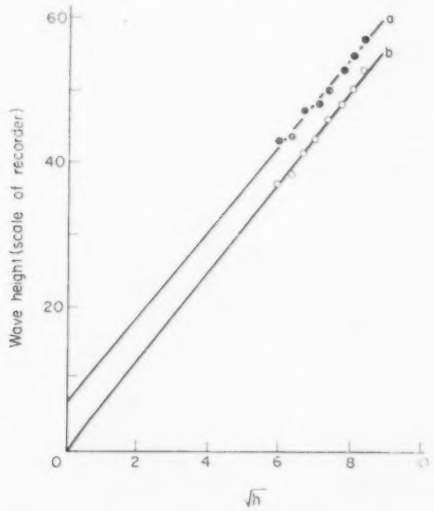

FIG. 2.—Relationship between wave height of the d.c. polarogram and $\sqrt{h}$.
(a) 1m*M* *p*-nitrophenol in 0·5*M* sodium carbonate solution
(scale, 20 = 12 μA)
(b) 1m*M* cadmium sulphate in 0·5*N* NH_4OH–0·5*M* NH_4Cl solution
(scale, 20 = 12 μA)
Temp. 25°

in sodium carbonate or trisodium orthophosphate solutions include the kinetic current are not solely diffusion-controlled.

(*ii*) *A.c. and d.c. polarograms in potassium hydroxide solution:* The a.c. and d.c. polarograms of *p*-nitrophenol show two reduction waves in potassium hydroxide solution as in the case of sodium carbonate or trisodium orthophosphate solution.

TABLE III.—HALF-WAVE POTENTIAL AND PEAK POTENTIAL OF *p*-NITROPHENOL IN POTASSIUM HYDROXIDE SOLUTION

Concentration of KOH, *N*		1	0·1
Peak potential, a.c. V	First wave	−0·915	−0·94
	Second wave	−1·45	−1·64
Half-wave potential, d.c. V	First wave	−0·97	−0·96
	Second wave	−1·53	−1·53

Table III gives the half-wave potentials and the peak potentials for *p*-nitrophenol in 1*N* and 0·1*N* potassium hydroxide respectively.

In Fig. 3, the polarograms (a) and (b) show the a.c. polarograms in 1*N* and 0·2*N* potassium hydroxide solutions and (a′) and (b′) show the d.c. polarograms in these solutions. From a comparison between them, it is found that the first "wave height"

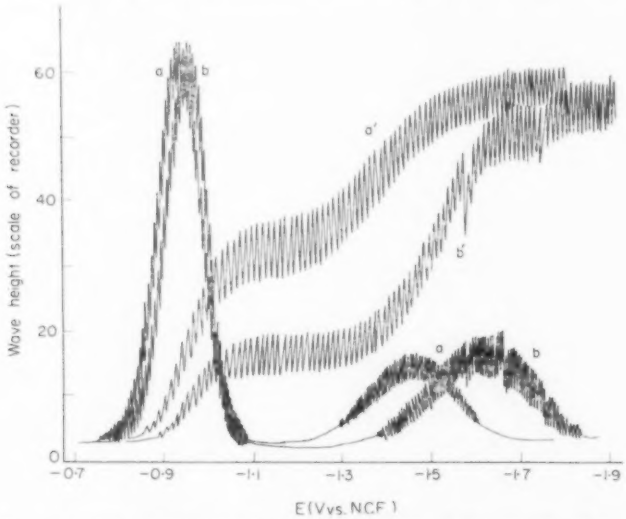

FIG. 3.—a.c. and d.c. polarogram of 1m*M* *p*-nitrophenol in potassium hydroxide solution
(a) a.c. polarogram in 1*N* KOH (scale,20 = 0·4 mV)
(a) d.c. polarogram in 1*N* KOH (scale, 20 = 12 μA)
(b) a.c. polarogram in 0·2*N* KOH (scale, 20 = 0·4 mV)
(b) d.c. polarogram in 0·2*N* KOH (scale, 20 = 12 μA)
Temp. 25°

is smaller than the second "wave height" in the d.c. polarograms but in the a.c. polarograms the first "wave height" is much greater than the second "wave height". The effect is more noticeable in more dilute potassium hydroxide solution. The first "wave height" in the d.c. polarograms increases with the concentration of potassium hydroxide, as with sodium carbonate or trisodium orthophosphate solutions (see Fig. 4). The first wave for the a.c. polarograms is unaffected by the concentration of potassium hydroxide (see Table IV).

The first "wave height" in the d.c. polarograms also increases with concentration

TABLE IV.—THE CHANGE OF THE FIRST-WAVE HEIGHT OF A.C. AND D.C. POLAROGRAMS WITH THE CONCENTRATION OF POTASSIUM HYDROXIDE

Concentration of KOH, *N*		0·2	0·7	1·0
The first "wave height"	a.c., mV	1·20	—	1·22
	d.c., μA	10·7	13·5	16·4

of salts such as potassium nitrate, sodium chloride, potassium bromide, added to 0·2*N* potassium hydroxide solution, but the "wave height" for the a.c. polarograms shows no change. The addition of 0·001 % gelatine has little effect on the first and second "wave heights" of the d.c. polarogram but suppresses the maximum phenomenon of the second wave.

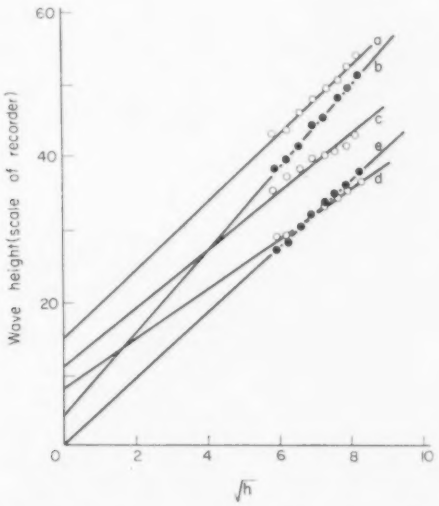

FIG. 4.—Relationship between wave height the of d.c. polarogram and $\sqrt{h}$
(1m*M* *p*-nitrophenol in KOH of various concentrations)
(a) in 0·2*N* KOH + 0·2*M* NaCl
(b) in 0·2*N* KOH
(c) in 1*M* KOH
(d) in 0·1*N* KOH + 0·9*M* NaCl
(e) in 0·1*N* KOH
(scale, 20 = 12 μA) Temp. 25°

Fig. 4 shows the relationship between the first "wave heights" of the d.c. polarograms of 1m*M* *p*-nitrophenol in potassium hydroxide solution and $\sqrt{h}$. The line (e), which refers to the d.c. polarogram in 0·1*N* potassium hydroxide solution, passes through the origin, so that the first wave of *p*-nitrophenol is solely diffusion-controlled in this solution. However, if 0·9*M* sodium chloride is added to 0·1*N* potassium hydroxide the line (d) deviates from the origin, showing the addition of the kinetic current to the diffusion current. This also applies to the d.c. polarograms in KOH solutions of higher concentration than 0·1*N*. From the relatively small change of the first "wave height" in a.c. polarograms it is evident that a.c. polarography is free from kinetic current.

(2) *m-Nitrophenol (in 1% methyl alcohol)*

A.c. and d.c. polarograms in potassium hydroxide solution: Fig. 5 shows the a.c. and d.c. polarograms of 1m*M* *m*-nitrophenol in potassium hydroxide solution. In 0·2*N* potassium hydroxide solution the d.c. polarogram (a) does not show the first and second waves distinctly, but the a.c. polarogram (a′) shows two distinct reduction waves (the first peak at −0·82 V, the second peak at −1·24 V v. NCE). However, in 1N potassium hydroxide solution, the a.c. and d.c. polarograms show the single wave (a.c. peak potential at −0·78 V, d.c. half-wave potential at −0·79 V). The wave height of the d.c. polarogram of *m*-nitrophenol is about two thirds that of *p*-nitrophenol

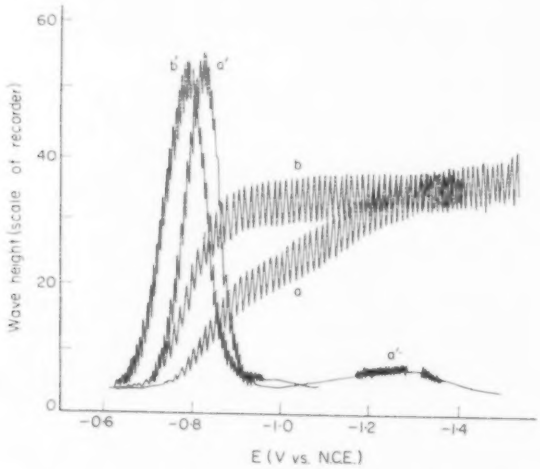

FIG. 5.—d.c. and a.c. polarograms of 1m*M* *m*-nitrophenol
(a) d.c. polarogram in 0·2*N* KOH (scale, 20 = 12 μA)
(a′) a.c. polarogram in 0·2*N* KOH (scale, 20 = 0·4 mV)
(b) d.c. polarogram in 1*N* KOH (scale, 20 = 12 μA)
(b′) a.c. polarogram in 1*N* KOH (scale, 20 = 0·4 mV)
Temp. 25°

under similar conditions, but the a.c. peak height of *m*-nitrophenol is equal to that of *p*-nitrophenol and does not change with the concentration of potassium hydroxide solution.

Also it was found that the d.c. polarogram of *m*-nitrophenol in 0.1*N* potassium hydroxide solution shows a single wave instead of two reduction waves when about 0.6*M* solutions of such salts as sodium chloride, or potassium nitrate are present.

Fig. 6 shows the relationship between the wave height of 1 m*M* *m*-nitrophenol in 0·5*N* ammonium hydroxide solution and $\sqrt{h}$. The line (a) passes the origin, but other lines (b), (c), (d) such as those in 0·5*N* ammonium hydroxide and 0.4*M* sodium chloride solution, 0·8*N* or 0·5*N* potassium hydroxide solutions, do not pass through the origin, so that they are contaminated with the kinetic current. As a check the polarography of 1m*M* cadmium sulphate in 0·5*M* ammonium chloride-ammonium hydroxide solution was examined soon after the above experiment and it was confirmed that the line for wave height plotted against $\sqrt{h}$ passed through the origin.

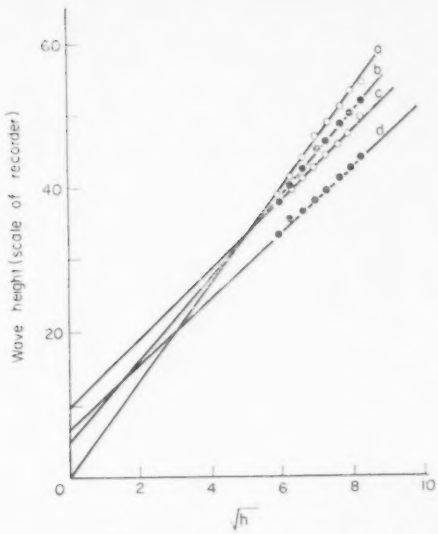

FIG. 6.—Relationship between the wave height of the d.c. polarogram of *m*-nitrophenol and $\sqrt{h}$.
(a) 1m*M* *m*-nitrophenol in 0·5*N* NH_4OH (scale, 20 = 8 μA)
(b) 1m*M* *m*-nitrophenol in 0·5*N* NH_4OH + 0·4*M* NaCl (scale, 20 = 8 μA)
(c) 0·5m*M* *m*-nitrophenol in 0·8*N* KOH (scale, 20 = 4 μA)
(d) 1m*M* *m*-nitrophenol in 0·5*N* KOH (scale, 20 = 8 μA)
Temp. 25°

(3) *o-Nitrophenol (in 1% methyl alcohol)*

(*i*) *A.c. and d.c. polarograms in potassium hydroxide solution:* Fig. 7 shows the a.c. and d.c. polarograms of 1 m*M* *o*-nitrophenol in 1*N* and 0·1*N* potassium hydroxide solutions. In 1*N* potassium hydroxide solution the d.c. polarogram (a′) is obviously a single wave (half-wave potential at −0·89 V) with a height almost equal to the total "wave height" of the d.c. polarogram of 1m*M* *p*-nitrophenol in 1*N* potassium hydroxide solution. The a.c. polarogram (a) of *o*-nitrophenol shows a lower peak height (at −0·92 V) than does either *p*- or *m*-nitrophenol, and for a concentration of less than 0·5*N* potassium hydroxide the a.c. polarogram (b) of *o*-nitrophenol shows two distinct reduction waves (the first peak at −0·88 V, the second peak at 1·01 V), while the d.c. polarogram (b′) shows still only a single wave (half-wave potential at −0·87 V).

(*ii*) *Relationship between wave height of d.c. polarograms in potassium hydroxide solution and* $\sqrt{h}$*:* Fig. 8 shows the relationship between the "wave height" of d.c. polarograms of 1m*M* *o*-nitrophenol in 0·2*N* potassium hydroxide or 0·5*M* ammonium chloride-ammonium hydroxide solution and $\sqrt{h}$. The lines (a) and (b) pass through the origin as indicated in Fig. 8 and it is confirmed that their limiting currents are evidently diffusion-controlled.

The d.c. polarogram of 1m*M* *o*-nitrophenol shows a lower "wave height" in acetic acid-sodium acetate solution (pH 4 ~ 6, the total amount of acetate ion being 0·5*M*) than in 0·2*N* potassium hydroxide solution. The relationship between the "wave heights" and $\sqrt{h}$ is given in curves (c), (d) and (e) in Fig. 8, which do not pass through the origin. However, at pH 9 the curve passes through the origin and the "wave

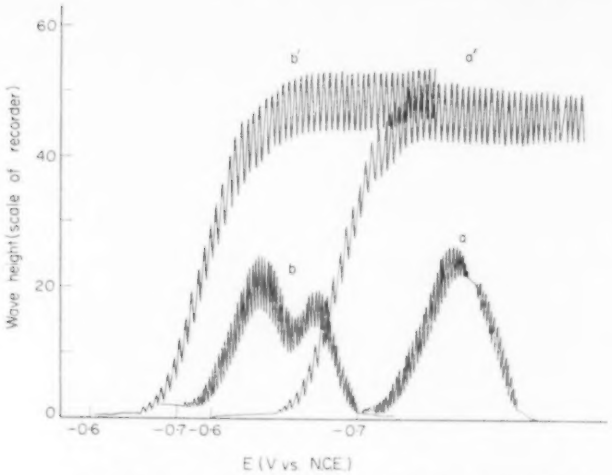

FIG. 7.—a.c. and d.c. polarogram of 1m*M* *o*-nitrophenol
(a) a.c. polarogram in 1*N* KOH (scale, 20 = 0·4 mV)
(a′) d.c. polarogram in 1*N* KOH (scale, 20 = 12 μA)
(b) a.c. polarogram in 0·1*N* KOH (scale, 20 = 0·4 mV)
(b′) d.c. polarogram in 0·1*N* KOH (scale, 20 = 12 μA)
Temp. 25°

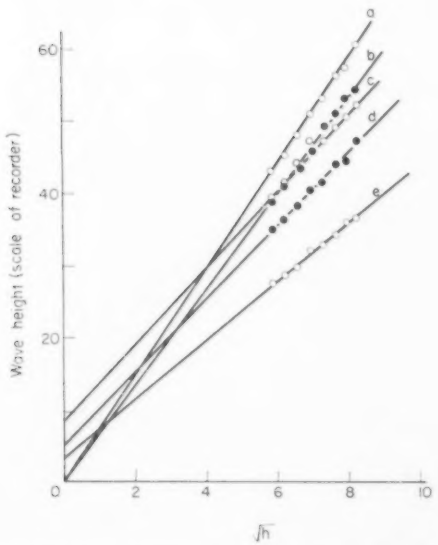

FIG. 8.—Relationship between wave height and $\sqrt{h}$ (1m*M* *o*-nitrophenol)
(a) in 0·2*N* KOH (scale, 20 = 12 μA)
(b) in 0·5*N* NH_4OH + 0·5M NH_4Cl (pH 9)
(c) in NaAc + HAc (pH 7) (scale, 20 = 8 μA)
(d) in NaAc + HAc (pH 4) (scale, 20 = 8 μA)
(e) in NaAc + HAc (pH 6) (scale, 20 = 12 μA)
Temp. 25°

height" is near that obtained in 0·2*N* potassium hydroxide solution. Therefore it is evident that the d.c. polarogram of *o*-nitrophenol is contaminated with the kinetic current in the range pH 4 ~ 7, but free of the kinetic current and solely controlled by diffusion at a pH above 9.

(*iii*) *Relationship between the "wave height" in a.c. polarograms and concentration of o , m-, and p-nitrophenol:* Fig. 9 shows the calibration curves for *o*-, *m*-, and *p*-nitrophenols in 0·2*N* and 2*N* potassium hydroxide solutions in the a.c. polarograms. The curves pass through the origin, and show a linear relationship between the concentrations of nitrophenol isomers and their "wave heights."

DISCUSSION

p-Nitrophenol is reduced on the electrode surface to *p*-aminophenol. *o*-Nitrophenol gives the same magnitude of wave height as *p*-nitrophenol at a pH above 9, so that it should be reduced to *o*-aminophenol in a parallel way to *p*-nitrophenol. But at a pH below 9, *o*-nitrophenol gives a low wave height so that the electrode reduction is apparently not so complete.[2] The present study shows that the reduction is not solely diffusion-controlled.

m-Nitrophenol shows a lower "wave height" than *p*-nitrophenol, which can be reduced completely to *p*-aminophenol. The present study shows that the reduction wave of *m*-nitrophenol is solely diffusion-controlled in 0·5*N* or 0·8*N* potassium hydroxide, and in 0·5*M* ammonium hydroxide and 0·4*M* sodium chloride solutions.

The d.c. polarograms of *p*-nitrophenol show two reduction waves in 0·2*N* ~ 1*N*

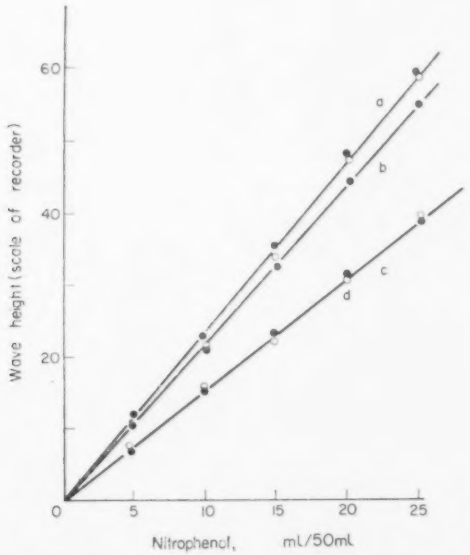

FIG. 9.—Calibration curves of nitrophenol isomers by a.c. polarography
(a) 2·5 m*M* *m*-, and 2 m*M* *p*-nitrophenols in 0·2*N* KOH (scale, 20 = 0·4 mV)
(b) 2 m*M* *p*-nitrophenol in 2*N* KOH (scale, 20 = 0·4 mV)
(c) 2 m*M* *m*-nitrophenol in 2*N* KOH (scale, 20 = 0·4 mV)
(d) 2 m*M* *o*-nitrophenol in 0·5*N* NH_4OH–0·5*M* NH_4Cl (scale, 20 = 0·2 mV)
Temp. 25°

potassium hydroxide solution and its first wave includes the kinetic current. Therefore it is considered that it is impossible to interpret the electrode reaction correctly since the reduction wave includes the kinetic current. Since the kinetic current refers to the relative rate of equilibration, it is concluded that in these solutions the isomers exist in different states, which are in mutual equilibrium.

From the viewpoint of analytical chemistry, a.c. polarography is more easily adapted for the polarographic determination of nitrophenol isomers than d.c. polarography, because the former is free from the kinetic current. There is a good linear relationship between the concentrations of the isomers and wave heights, which does not change with the concentration of supporting electrolytes such as potassium hydroxide.

Zusammenfassung—Die Wellenhöhe in Wechselstrompolarogrammen von *o*-, *m*- und *p*-Nitrophenol in Kaliumhydroxyd oder Amoniumchlorid-Ammoniaklösung sind nahezu proportional der Konzentration. Verschiedene Reduktionswellen im Gleichstrompolarogramm sind durch kinetische Ströme stark gestört. Da dies in der Wechselstrompolarographie nicht der Fall ist, kann letztere sehr vorteilhaft zur Analyse von Gemischen der Nitrophenolisomere herangezogen werden.

Résumé—Les hauteurs de vague des polarogrammes en courant alternatif des *o*-, *m*- et *p*-nitrophénols sont exactement proportionnelles à leur concentration en solution de potasse ou ammoniaque-chlorure d'ammonium. Plusieurs parmi ces vagues de réduction dans les polarogrammes en courant continu sont gênées par le courant cinétique. Celui-ci n'apparaît pas normalement en polarographie à courant alternatif; cette dernière méthode est beaucoup plus pratique pour le dosage des isomères du nitrophénol.

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THE SEPARATION OF SUB-MICROGRAM AMOUNTS OF URANIUM FROM MILLIGRAM AMOUNTS OF IRON, ALUMINIUM AND PLUTONIUM

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Summary—A separation procedure has been developed to facilitate the fluorimetric determination of sub-microgram quantities of uranium in the presence of milligram amounts of iron, aluminium and plutonium. The sample is mixed with a strong hydrochloric acid solution containing hydriodic acid and passed through a column of anion-exchange resin. Only the uranium is retained on the resin and it can subsequently be eluted with dilute hydrochloric acid.

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INTRODUCTION

THE separation described was developed to meet a requirement for the determination of the uranium content of solutions containing 0·05–1·0 μg of uranium per ml in 1–2M nitric acid containing 0·02–0·03M iron, 0·01M aluminium and 0·001–0·005M plutonium. The uranium content of such solutions can be determined by direct fluorimetry[1] but two factors militate against this approach. Firstly, the concentration of the major components of the solution is sufficient to cause considerable quenching of the uranium fluorescence[2] and correction for this tends to be inaccurate at the low concentrations of uranium involved. Secondly, the presence of plutonium limits the size of the sample aliquot which can be handled without resort to glove-box working, and this in turn limits the attainable sensitivity of the procedure.

For the above reasons, a procedure for separating the uranium from the interfering ions was desirable. The method selected is based upon the fact that if the sample is made 10–11M in hydrochloric acid in the presence of a suitable reducing agent the contaminants will be present as iron^{II}, aluminium^{III} and plutonium^{III}, all of which will pass unadsorbed through an anion-exchange resin column under these conditions, whereas uranium^{VI} will be retained by the resin and can subsequently be eluted with dilute hydrochloric acid.[3] Hydriodic acid proved to be a suitable reducing agent, and this system, with minor modifications to improve de-contamination from iron, yielded pure solutions of uranium ideally suited for fluorimetric analysis.

EXPERIMENTAL

Reagents

Test solution: Preliminary experiments were carried out using a synthetically prepared stock solution having the composition: 0·1 μg of uranium/ml, with 0·004M plutonium, 0·03M iron^{II}, 0·015M iron^{III} and 0·01M aluminium in 1·5M nitric acid.

11M *Hydrochloric acid*/7% *hydriodic acid:* This eluent was chosen, since earlier experience had shown that it gave efficient conversion of plutonium to the tervalent state and effectively separated plutonium from uranium on the resin column. It was necessary to remove iodine from commercial hydriodic acid before incorporating it in the eluent. This was achieved by passing the commercial solution through a column (20 cm × 0·6 cm) of Deacidite FF in the chloride form. The life of the column could be prolonged by first removing the bulk of the iodine, by shaking the hydriodic acid with

several g of resin in a beaker. The 11*M* hydrochloric acid/7% hydriodic acid was prepared freshly shortly before use.

Ion-exchange columns

Columns were prepared in glass vessels, approximately 10 cm in length and of 0·4-cm outer diameter, fitted with a reservoir of some 10-ml capacity at the top and with a tap at the bottom. The resin, Deacidite FF, was air-dried and ground to pass 60–80 mesh, and 0·5 g was packed into each column. The resin was conditioned to the chloride form and treated with 11*M* hydrochloric acid immediately before the addition of each sample. Use of the hydrochloric acid/hydriodic acid eluent resulted in the formation of iodine which was taken on the resin. This could be removed with some difficulty by washing the resin with sodium hydroxide but, in general, replacement of the resin as necessary was preferred.

Fluorimetric analysis

The uranium eluate, usually 4 ml, was divided into two equal portions, each of which was evaporated to dryness in 1-ml lots in a platinum capsule under an infrared heater. To one of these capsules was added 0·2 μg of uranium from a standard solution to serve as an internal calibration. Each capsule was then fused in an oven at 850 $\pm$ 20° with 0·6 g of flux (90% sodium bicarbonate/10% sodium fluoride) for 5 min. After cooling for 5 min, the fluorescence of each capsule was read in a Harwell Type 1080A fluorimeter.

Separation procedure

To test the effectiveness of the separation procedure, several experiments were performed as follows. One ml of the test solution was pipetted into 2 ml of 11*M* hydrochloric acid/7% hydriodic acid contained in the column reservoir. The solutions were mixed and allowed to flow through the column at a rate of 0·4 ml/min. The column was washed with a further 1 ml of the mixed acids and the uranium eluted with varying volumes (1–4 ml) of 0·1*M* hydrochloric acid. The uranium content of the eluates was determined fluorimetrically.

RESULTS AND DISCUSSION

The eluates were contaminated with iron, which caused quenching of the uranium fluorescence, and precluded accurate determination of the amount of uranium recovered. Recoveries were therefore established by the use of a uranium-233 tracer.

Table I.—Recovery of 0·1 μg of uranium-233 in the absence of other cations

Volume of eluate (0·1*M* HCl) collected, *ml*	Total amount of uranium eluted, μg
1	0·056
2	0·088
3	0·094
4	0·099

Table II.—Recovery of 0·1 μg of uranium-233 from test solution

Experiment No.	1	2	3	4	5	6
Uranium recovered, μg	0·096	0·090	0·075	0·080	0·10	0·084

α-Counting of the hydrochloric acid eluates showed a good recovery of the uranium-233, both alone and in the presence of the test solution, and also indicated that 4 ml

of 0·1 *M* hydrochloric acid adequately eluted the uranium. Typical results are given in Tables I and II. The aluminium content of the eluates was shown by the aluminon method[4] to be less than 5 μg.

The presence of iron in the uranium eluates is due to incomplete reduction, since iron^{II} is not adsorbed on anion-exchange resins from chloride solutions.[5] 11 *M* Hydrochloric acid/7% hydroxylamine hydrochloride, 11 *M* hydrochloric acid/7% hydrazine hydrochloride and 9 *M* hydrochloric acid/7% ascorbic acid were tried as alternatives to 11 *M* hydrochloric acid/7% hydriodic acid in attempts to improve the efficiency of the reduction of iron^{III}, but without success. Evidently efficient reduction to iron^{II} occurs only at lower chloride concentrations where complexing of the iron^{III} by chloride is less complete. Maximum removal of iron should be obtained by incorporating an intermediate column wash, using the reducing agent in hydrochloric acid of concentration as low as possible consistent with maintaining the uranium completely in the resin phase. It was demonstrated that a 2-ml wash with 4 *M* hydrochloric acid/7% hydriodic acid removed iron almost completely from the column

TABLE III.—APPLICATION OF METHOD TO 1 ML OF TEST SOLUTION

Uranium recovered, μg	0·08, 0·09, 0·13, 0·14, 0·11, 0·13, 0·10 0·11, 0·08, 0·08
Column blank, as μg of uranium	0·01, 0·006, 0·009, 0·008

without prejudicing the good recovery of uranium. Subsequent elution of uranium yielded solutions of sufficient purity to eliminate quenching in the fluorimetric analyses which followed.

The following procedure has been used successfully both on aliquots of the test solution and on a considerable number of sample solutions:

Procedure

Add 1 ml of the relevant solution to 2 ml of 11 *M* hydrochloric acid/7% hydriodic acid in the column reservoir. Mix the solutions and allow them to flow through the column at 0·4 ml/min. Wash the column with 1 ml of 11 *M* hydrochloric acid/7% hydriodic acid followed by 2 ml of 4 *M* hydrochloric acid/7% hydriodic acid at the same flow rate. Elute the uranium from the column with 4 ml of 0·1 *M* hydrochloric acid, again at 0·4 ml/min, and subject the eluate to fluorimetric analysis by the standard procedure. Perform occasional blank determinations on the column using the above procedure in the absence of uranium.

Table III shows a number of results obtained using the test solution; evidently 0·02 μg of uranium per ml represents a reasonable lower limit for the method.

α-Counting of the uranium eluates showed that the plutonium content was in all cases less than 0·4 μg, representing a decontamination over the column of better than 2000.

A number of samples were received in which the foreign ion concentrations were appreciably lower than those quoted for the test solution. Such samples were analysed by direct fluorimetry and corrected for quenching effects[1] as well as by the ion-exchange procedure. The results are shown in Table IV and indicate satisfactory agreement in all cases.

Clearly the method will separate uranium from other elements in addition to

iron, aluminium and plutonium, the criterion for separation being that the element, or a lower valency state thereof, does not form chloride complexes which can be adsorbed on the anion-exchange resin. The most serious interference is likely to be due to complexing anions. Such interference has not been systematically studied, but it has been noted during the present work that sulphate at a concentration of 0·05*M* produces no interference.

Table IV.—Comparison of direct fluorimetry and ion exchange/fluorimetry

Sample No.	Uranium concentration by ion-exchange method, *μg/ml*	Uranium concentration by direct method, *μg/ml*
1	0·65	0·60
2	0·30	0·27
3	0·06	0·05
4	0·10	0·06
5	0·64	0·67
6	0·02	0·02

Acknowledgement—Some of the results given in Table IV were obtained by Messrs. E. B. Astridge and W. Dobbins.

Zusammenfassung—Eine Trennungsmethode wurde entwickelt um die fluorimetrische Bestimmung von Submikrogrammengen Uran in Gegenwart von Milligrammengen Eisen, Aluminium und Plutonium zu erleichtern. Die Probe wird mit einer Jodwasserstoff enthaltenden, starken Salzsäure gemischt und durch eine Anionenaustauschersäule geschickt. Das Uran wird in der Säule zurückgehalten und anschliessend mit verdünnter Salzsäure eluiert.

Résumé—Les auteurs ont mis au point une méthode de séparation pour faciliter le dosage fluorimétrique de quantités inférieures au microgramme d'uranium en présence de quantités de l'ordre du milligramme de fer, d'aluminium et de plutonium. L'échantillon est mélangé avec une solution d'acide chlorydrique concentré contenant de l'acide iodhydrique et on le fait passer sur une colonne de résine échangeuse d'anions. Seul l'uranium est retenu sur la résine, il peut être ensuite élué par de l'acide chlorhydrique dilué.

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THE DETERMINATION OF OXYGEN, HYDROGEN, NITROGEN AND CARBON IN METALS

A REVIEW

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Summary—A review of the methods for determining oxygen, hydrogen, nitrogen and carbon is presented. Recent developments in apparatus and techniques which have contributed materially to more precise and high speed analyses are discussed. Inert gas fusion is reviewed, together with recent advances that have contributed towards making this apparatus a very flexible and excellent control tool. Since a large number of metals require a bath or flux in which to alloy the sample, a critical review is presented of the platinum bath, platinum flux, and intermittent bath injection methods. Recommendations for further development are for methods which are capable of analysing high purity metals containing less than 10 ppm, and for methods where the amount of sample is limited. Also new methods or techniques should be investigated for the determination of nitrogen in metals, especially in the refractory metals and alloys.

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MOST metals contain measurable amounts of carbon, oxygen, hydrogen and nitrogen which have been introduced through processing *i.e.*, melting, rolling, annealing, etching, *etc.* In order to meet specifications for a given application, it is necessary to establish the order of magnitude of these impurities. Since the materials vary greatly in their impurity level, the selection of the most suitable analytical method is of prime importance. The apparatus selected should, under ideal circumstances, be based on the following criteria:

1. Sensitivity
2. Range
3. Adaptation to impurity
4. Availability of apparatus
5. Speed of analysis
6. Cost.

Several methods have been proposed and used for measuring the gas content of metals. Most of these methods are limited to the determination of oxygen only.

Solution method

This method[1] is based on the solution of the metal to leave the insoluble metal oxide. Cunningham and Price[2] investigated this technique for the determination of oxygen in iron, and encountered some difficulty because of the formation of insoluble iron compounds. Samples weighing 5–10 g were agitated in a solution of iron^{II} iodide. Further separations and determinations of the silicon, manganese, iron and aluminium content of the residue were required before a calculation could be made. The method is most adaptable to samples of high oxygen content and provides results which give an estimate of the metallic composition of the oxide.

Evolution method

This method is based on the vaporisation of the metal at 800° in a stream of chlorine. The residual metal oxide is weighed. The method is adaptable to metals of relatively high oxygen content. Lilliendahl, Wroughton and Gregory[3] applied this technique to the determination of oxygen in zirconium. The method is subject to many corrections rendered necessary by side reactions such as that between carbon and metal oxide. Also, contamination of the oxide by other metal oxides requires a correction based on an initial impurity analysis. The precision is only about 0·02% based on a 2-g sample. This method still has some applications but, in general, it has been replaced by more precise techniques.

Bromination method

In this method[4] the metal sample is heated with graphite, in a stream of helium or argon and bromine. In this manner, the oxygen is converted to carbon monoxide. The bromine and volatile metal bromides are removed in dry-ice traps. The carbon monoxide is oxidised to carbon dioxide, absorbed in Ascarite and weighed. This method is adaptable to the determination of oxygen in metals in the range of 100 to 5000 ppm.

Emission spectrometric method

The metal sample is excited in an inert atmosphere of argon with a d.c. carbon arc.[5] The method is rapid, and has been found to give results comparable with those from the vacuum fusion method when applied to the determination of oxygen in refractory metals. Further extension of this method through refinements in technique and apparatus may result in its application to determine low concentrations.

Isotope dilution method

The sample is heated with a measured amount of ^{18}O introduced as an isotope-enriched metal powder. The sample and the enriched alloy are heated in a graphite crucible to establish an equilibrium of oxygen-16/oxygen-18. At the point of equilibrium, the oxygen-16/oxygen-18 ratio is identical in all compounds and phases. The new diluted ratio is measured with a mass spectrometer. The method offers one main advantage over fusion methods in that a complete removal of the oxygen is not necessary. The technique[6] is in limited use for metals because it requires a good high vacuum apparatus for establishing the equilibrium in addition to a mass spectrometer for analysis. However, since stable isotopes are available for nitrogen as well as for oxygen, the method offers several unique applications. The best lower limit approximates to 10 ppm.

Activation method

This method[7] is based on surrounding the sample with lithium fluoride during irradiation by neutrons generated from a pile. The neutron reaction $^{6}Li(n,\alpha)^{3}H$ produces a source of tritons, ^{3}H. These tritons activate the oxygen nuclei in the sample to produce ^{18}F by the secondary reaction $^{16}O(^{3}H,n)^{18}F$. The ^{18}F decays by positron emission. The positrons are accompanied by annihilation γ-radiations which

are used to complete the analysis by γ-scintillation spectrometry. The general use of this method is restricted because of the requirement of a strong neutron source. The method is not suitable for the determination of trace quantities of oxygen, hydrogen and nitrogen, since these elements have a low probability of neutron absorption or a very short half-life for the radioactivity. Metals have been analysed for oxygen by this technique in the range of 10 ppm and above.

Infrared absorption method

The presence of dissolved oxygen in a semi-conductor may affect infrared absorption. Kaiser, Keck and Lange[8] found that there was an absorption band at 9 μ in silicon which corresponded to the asymmetric silicon-oxygen stretching bond vibration. Similarly, there is an absorption band at 11·7 μ corresponding to oxygen in germanium.[9] These are the only two semi-conductors that have been studied by this method. The method was calibrated by vacuum fusion. This technique has been applied to samples containing 20 ppm of oxygen or less, with good sensitivity in the low concentrations. It has been applied to single crystal material.

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Inert gas fusion

The metal sample may be melted in a graphite crucible, in an inert atmosphere of argon. The oxygen in the sample is converted to carbon monoxide, which is oxidised to carbon dioxide. The carbon dioxide formed may be absorbed in Ascarite and weighed, or even better, may be absorbed in dilute barium hydroxide. The change in conductivity of the barium hydroxide solution is measured as a function of the oxygen content. A calibration curve is established by fusing a known amount of an oxygen standard and measuring the resistance change. From this curve, the oxygen content of the sample can be determined. The method is applicable to samples containing oxygen from 10 ppm upwards, but it is more generally used for oxygen in excess of 50 ppm. The procedure is rapid, and very suitable for control work.

Vacuum fusion method

On fusing the metal sample in a graphite crucible, in vacuum, the oxygen in the sample is converted to carbon monoxide, and hydrogen and nitrogen are evolved. Provisions are made for determining the gas composition. This is the most versatile tool, since it can measure and analyse the total gas. Also, it currently is the most sensitive. This feature makes it possible to analyse high purity materials or samples when the amount available is limited. The most satisfactory working range is from 10 to 2000 ppm. Some investigations have been carried out at 10 ppm and below through special refinements in technique.

Hot extraction method

In many instances the measurement of the hydrogen content of the metal is of sole importance. This measurement is most readily made by hot extraction. The principle of the method is based on extracting the hydrogen from the metal by heating in vacuum at about 1200°. The hydrogen evolved is collected and measured. For samples which give small amounts of other gases in addition to hydrogen, provisions

are made for their separation from the hydrogen. The analysis time is generally of the order of 30 min per sample.

Determination of carbon

Most metals contain measurable amounts of carbon and oxygen, and when heated evolve either carbon dioxide, carbon monoxide or both, depending on the temperature. This reaction should be given the utmost attention in fundamental studies of materials used in electronic devices. Since the presence of carbon in metals can be detrimental in some applications, and very necessary in others, it becomes of prime importance to make a quantitative measurement of the carbon content as well as of the oxygen.

The principle of the measurement of carbon depends on the combustion of the metal sample in oxygen, with the separation and measurement of the carbon dioxide. The carbon dioxide may be measured by absorption in Ascarite and weighing, volumetric absorption in caustic potash to measure the amount of carbon dioxide absorbed, or absorption in caustic potash and measuring the change in conductivity, or separation by freezing out in liquid nitrogen. In the last case, the carbon dioxide is frozen out in liquid nitrogen, the excess oxygen is removed to vacuum pump, and the carbon dioxide pressure is measured in a known volume. Currently, the conductivity method is most widely used because of its speed, range and sensitivity. The low pressure combustion method is most applicable to the determination of carbon of a few ppm, or when a limited amount of sample is available.

Recent developments

Among the methods described above, vacuum fusion, inert gas fusion, hydrogen by hot extraction, and conductimetric carbon analyses are currently being widely used. As a result of the efforts of several gas metal groups which have carried out co-operative analyses, the range, sensitivity and accuracy of these methods have been constantly improved.

Inert gas fusion

While inert gas fusion is not new,[10] the method has developed into an exceilent high speed analytical tool for determining oxygen in metals. Smiley[11,12] carried out the fusion in a graphite crucible, in an atmosphere of argon. The argon acts as a carrier gas. The carbon monoxide formed from the fusion is oxidised to carbon dioxide. The carbon dioxide is frozen out in the capillary trap with liquid nitrogen, the argon is removed by a vacuum pump, and the carbon dioxide pressure is measured in the gas phase, in a known volume. This procedure requires about 12 min per determination. The Leco Co.* modified and improved this technique by combining inert fusion with a conductimetric method for measuring the carbon dioxide. The apparatus is shown schematically in Fig. 1. The carbon dioxide is absorbed in dilute barium hydroxide, and the change in conductivity is measured. This method offered a new and rapid approach to determining oxygen in metals. The analysis time is about 8 min.

Recently, experimental work has shown that the application of this method can be extended beyond the recommended scope.

* Laboratory Equipment Co., St. Joseph, Michigan, U.S.A.

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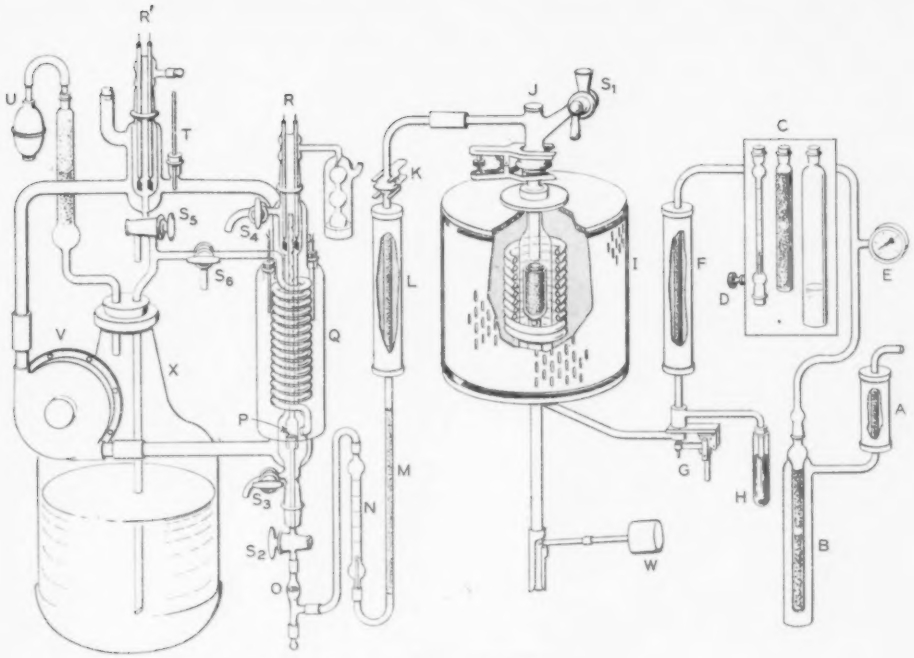

FIG. 1.—Inert gas fusion apparatus

A—Copper oxide

B—Magnesium perchlorate–Ascarite

C—Sulphuric acid, magnesium perchlorate, Ascarite and flow meter

D—Needle valve

E—Pressure gauge

F—Titanium metal

G—Quick disconnect

H—Mercury pressure release

I—Induction furnace quartz tube, containing graphite crucible floating in lamp block

J—Optical flat

K—Ball joint

L—Iodine pentoxide

M—Sodium thiosulphate

N—Flow-meter

O—Porous frit and mercury trap

P—Porous frit

Q—Water jacket, thermostated

R—Measuring cell

R'—Reference cell

S—S_2, S_3, S_4, S_5, two-way and S_6 three-way stopcocks

T—Thermometer

U—Aspirator bulb

V—Circulating pump

W—Weight

X—Carboy containing barium hydroxide

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1. *Calibration.* It has been customary to set up a standard calibration curve by fusing 2–4 mg of silver oxide in the graphite crucible and measuring the change in conductivity due to the carbon dioxide. Because of the inherent problems in handling such small amounts of silver oxide, the use of potassium hydrogen phthalate[13] offers a new, faster and accurate manner in which to prepare oxygen standards. In order to prepare these standards, several concentrations of potassium hydrogen phthalate are prepared in distilled water. A measured amount (0·2 ml) is transferred with a microsyringe* to tin cups having a volume >0·2 ml. These cups are placed in holes in a metal block and evaporated to dryness at a temperature not to exceed 100°. After evaporation to dryness, the tin cups are flattened with a spatula and rolled into a compact form. In this way, standards containing 10 to 2000 μg of oxygen can be readily prepared and stored for future use. In Fig. 2 is shown a typical calibration curve up to 1600 μg of oxygen, where the barium hydroxide concentration is 15 g/18

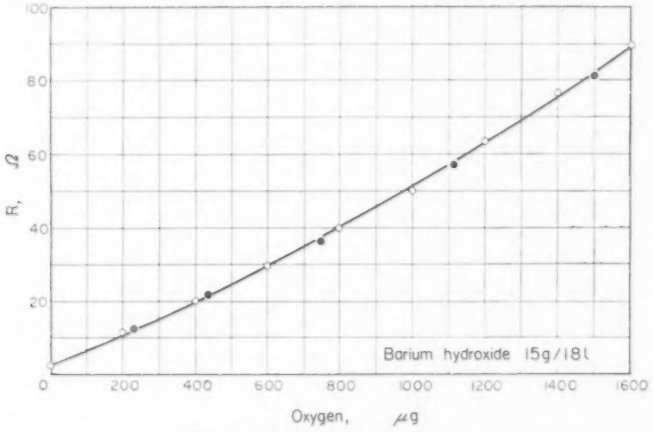

FIG. 2.—Standard calibration curve
○ Potassium hydrogen phthalate
● Silver oxide

litres. Each point on the curve represents an average of two to five determinations. The points obtained with potassium hydrogen phthalate are in good agreement with those obtained with silver oxide. Over this entire range, 0–1600 μg of oxygen, there is a deviation from a straight line relationship. This deviation is negligible over any 400-μg portion of the curve.

2. *Extending the application and range.* Initially, it was recommended that the method be applied to determinations in the range of 100–400 μg of oxygen. This was accomplished simply by adjusting the sample size. It is evident from Fig. 2, that any 400-μg portion of the curve is equally good. Therefore, it is advisable to run the sample first, then establish a calibration point on each side of the sample. A straight line drawn between these points (400-μg range) will introduce a negligible error.

In some instances where the oxygen content is high *e.g.*, ferrites, it is still not possible to reduce the sample size sufficiently to fall in a good working range. However, these high oxygen materials can be readily analysed by inert fusion, by substituting an Ascarite absorption tube for the conductivity cell. Samples weighing about 50 mg will give a weight gain of 40 mg of carbon dioxide, since one oxygen is picked up from the

* Microsyringe–0·25 ml micrometer adjustment—Scientific Glass Apparatus.

iodine pentoxide in the oxidation of the carbon monoxide to carbon dioxide. In carrying out reductions on ferrites, it is necessary to drop the sample into the crucible at ambient temperature, then switch on the induction heater to bring the temperature to 1650°. The reduction takes place at a sufficiently high temperature to favour the formation of carbon monoxide, yet slowly enough to prevent overloading the oxidising reagent and blowing the sample out of the crucible.

Currently, several gas metal studies have required the measurement of oxygen below 50 ppm. This has been found to be especially true in working with materials for electronic devices. When small amounts of oxygen are being determined, the barium hydroxide can be diluted. The barium hydroxide solution used for this work contains only 5 g/18 litres. A resistance change of 1 Ω is equivalent to only 1 or 2 ppm. In this manner, it is now possible to determine oxygen rapidly in metals below 50 ppm with a standard deviation of about 3 ppm.

One outstanding advantage of this method is that the fusion is carried out in an inert atmosphere. The argon gas suppresses the vapour pressure of the metals and prevents excessive deposition on the walls of the furnace. This opens an entirely new field of study by making it possible to determine the gas content of metals which have a high vapour pressure, heretofore not amenable to vacuum fusion. For example, metal oxides of aluminium and zinc can be quantitatively analysed.

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Hot extraction method

It has been found that hydrogen present in metals may have a marked affect on the ductility. Also, "hydrogen embrittlement" has been associated with failure of metal parts. Surface blistering and blow holes have also been found to be related to the hydrogen content.

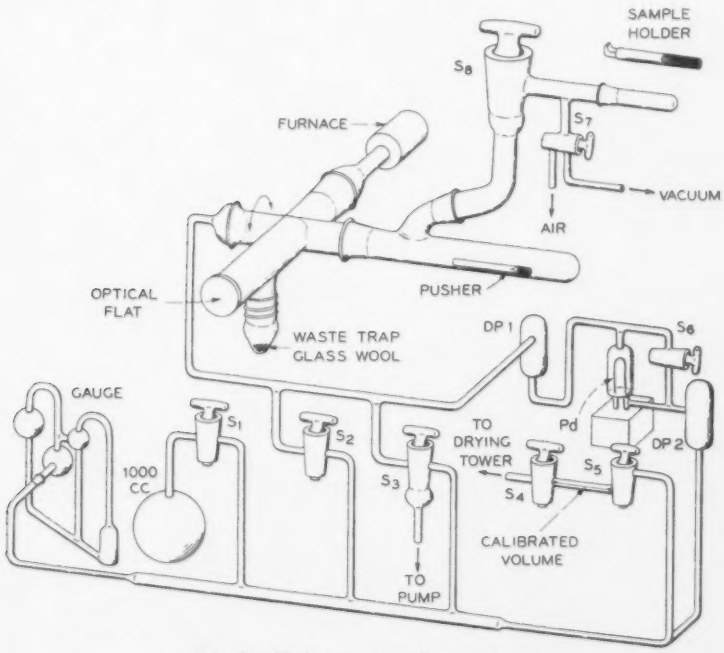

FIG. 3.—Hydrogen extraction apparatus.

Since many of the metals lose their hydrogen on standing, especially in vacuum, it is necessary to analyse these samples as rapidly as possible. This factor necessitates the injection of the sample into the apparatus for immediate analysis. Most units for measuring hydrogen have a vacuum lock which permits the immediate injection of the sample into the pre-conditioned analytical station. In Fig. 3 one unit is shown which is now commercially available.* One feature of this apparatus is the introduction of the sample for analysis through a vacuum lock. The sample is placed in the glass boat, which is inserted through the tapered joint. The cap is replaced and is made vacuum tight with Apiezon wax, W. The air about the sample is evacuated by opening stopcock S7 to vacuum. After the evacuation, S7 is closed and S8 is opened to the apparatus. The sample boat is pushed by means of a glass-enclosed metal slug through the hole in the stopcock. By rotation of the magnet, the sample is dropped without danger of contamination from the grease on the stopcock. A second magnetic pusher propels the sample into the furnace area. The furnace is rotated on a ball and tapered joint to inject the samples into the hot zone, and to reject them to the waste trap after analysis. In this way several samples can be analysed consecutively. During the hot extraction of the hydrogen, small amounts of carbon monoxide, carbon dioxide and nitrogen are evolved. The hydrogen is rapidly separated from these gases by diffusion

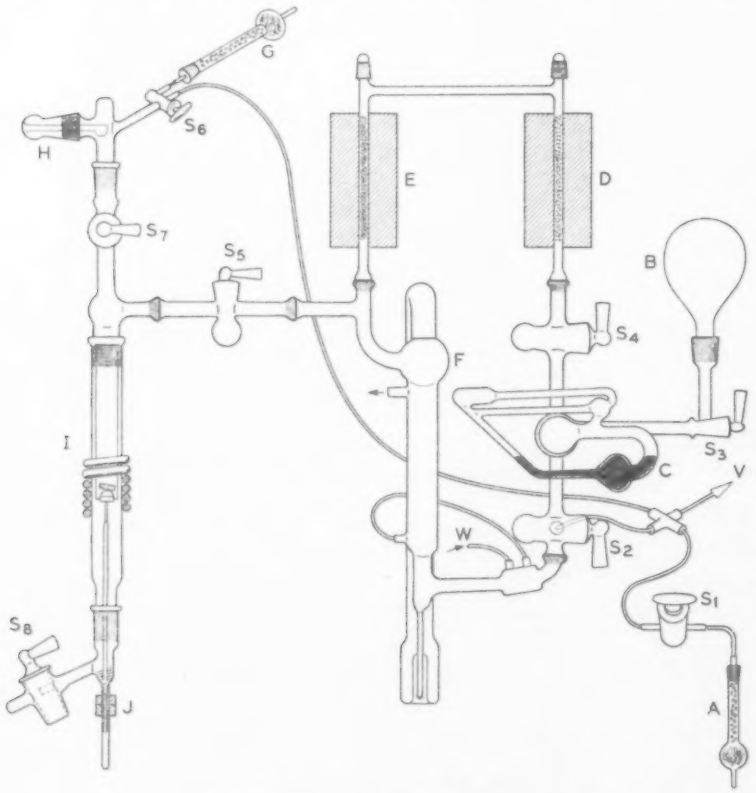

FIG. 4.—Hydrogen extraction apparatus.

* Fisher Scientific Co., Fisher-Serfass Hydrogen Analyzer

through a palladium valve or lamp. The hydrogen is collected with a diffusion pump, and is measured in a known volume by means of a Lippincott type of pressure gauge. The analysis requires about 10–30 min with a sensitivity of about 0·1 ppm.

Another apparatus* for determining hydrogen, shown in Fig. 4, employs a vacuum lock and a special stopcock with metal insert and guide tube for admitting the sample free from contamination into a vertical furnace. Also, the crucible has a false bottom operated up and down by means of a solenoid. This simple and unique feature makes it easily possible to reject a sample from the crucible after analysis. In this way, several samples can be analysed consecutively. In some instances, gases like O_2, N_2, CO and CO_2 may be evolved along with the hydrogen. In this apparatus, the total gas evolved is measured. Provisions have been made for circulating the gas mixture over copper oxide and magnesium perchlorate when it is considered necessary. The total gas is re-measured, and the difference is due to the hydrogen.

Vacuum fusion

The vacuum fusion method for analysis of the total gas content of metal samples is widely used, since it can be applied to almost all kinds of materials. Since the development of the high temperature all-glass fusion furnace, no major change in the equipment has developed. Most laboratories use equipment similar to the one manufactured by National Research Corporation.†

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In the past five years, through the co-operative efforts of many laboratories and gas-metal panels associated with A.S.T.M. and the technical branches of the armed services, considerable progress has been made in developing better techniques and understanding of fusion analyses. The most outstanding advances are as follows:

1. Application of the platinum bath and platinum flux techniques.
2. Intermittent bath injection.
3. A study of the sorption of gas by films deposited on the furnace walls during fusion analyses.

1. *Application of the platinum bath and platinum flux techniques.* Many metals and alloys, especially the refractory ones with high melting points, require a flux to remove the gas quantitatively. Initially, platinum was used as a bath into which samples were dropped for analysis.[12,14,15,16] Through co-operative analyses it was soon realised that the platinum bath technique could give trouble after several analyses, due to the formation of graphite flakes in the platinum melt.[17] It was found that this prevented proper alloying of the sample and quantitative recovery of gas. Since the oxygen content of platinum is relatively low (about 10 ppm) as compared with the gas content of the samples, fusion analyses can be carried out by injecting the sample and the platinum simultaneously. This method is referred to as the flux technique. The platinum flux technique offers several advantages. The platinum metal has a low vapour pressure which minimises the amount of metal evaporating to the furnace walls. This factor makes it possible to carry out fusions at high temperatures. By adding the flux with the sample, the analysis time is greatly reduced. Also, the danger of developing viscous and semi-fluid fusion baths is eliminated. For the best results, the platinum : sample ratio should be about 10 : 1, and both should be injected simultaneously. The platinum is used in rod, sheet or wire form. The last two forms

* Hydrogen Analyzer—Manufactured by Laboratory Equipment Co., St. Joseph, Michigan, U.S.A.
† National Research Corporation, Cambridge, Massachusetts, U.S.A.

can be wrapped tightly about the sample. In some analyses, tin has been added in small amounts, and has been found to be of some advantage, even though it contributes to the blank. The method is widely used for determining oxygen in refractory metals and alloys. The determination of nitrogen in refractory metals appears to be quantitative when platinum is used. Further study is required through co-operative laboratory analyses to establish if the removal of nitrogen is quantitative, by comparing the values with those obtained by the Kjeldahl method. The platinum is readily recovered from the fusion melt, and most laboratories return the fused ingots to the platinum manufacturer for reclaiming.

2. *Intermittent bath injection.* The use of iron as a fusion bath has been widely accepted by most laboratories for many years. One disadvantage of using iron is that it has a relatively high gas content. In view of this it is necessary to outgas the iron thoroughly, and then to determine a blank before dropping in a sample. These steps are time consuming. In many instances, variable results were obtained when this type of bath was used. McDonald, Fagel and Balis[18] showed that satisfactory recovery of gas could be obtained from a fluid iron bath. Since it was necessary to heat the iron bath to 1800° for metals having a high melting point, carbon dissolved in the iron to such an extent that the melt became viscous. This resulted in poor alloying of the sample and recovery of gas. Sloman and Harvey[19] recognised this problem, and made a point of keeping the bath temperature as low as possible and completing the reduction of the oxide within 20 min. Smith[20] showed that the iron bath is semi-solid within 2 hr at 1800° due to the formation of large graphite flakes. The greatest concentration of these flakes is nearest the top, which makes it difficult for the sample to alloy properly. The higher the temperature, the more rapid is the solution of carbon. When considerable carbon has dissolved in the ingot, gas evolved from the sample can be trapped in the semi-fluid melt below the viscous layer. The addition of tin appeared to be advantageous to minimise the loss of gas due to "gettering" by the evaporated metal films on the furnace wall. Beach and Guldner[21] showed that the periodic addition of iron and tin was a real advantage. The periodic addition of iron* was made after every other sample. The gas from the iron was removed to pump before the samples were analysed. The function of the tin is two-fold: firstly to increase the fluidity of the bath, and secondly to act as a mechanical stirrer. Due to the high vapour pressure of the tin at fusion temperature, the tin will boil off, stirring the molten bath. This technique minimises the danger of gas being entrapped in the iron bath. Without doubt, the iron bath used in this manner is the most satisfactory and most widely applicable fusion bath. It is applicable to all of the high melting point and refractory type metals.

3. *Sorption of gas by metal films deposited on the furnace walls.* It is inherent in vacuum fusion analyses that carbon and metal vapours deposit on the glass walls of the furnace. It is certain that many investigators have felt that some of the gas evolved from the sample was re-adsorbed on these films. In the earlier years of vacuum fusion these losses would probably have been negligible since the gas levels were comparatively high; hence no comprehensive study was carried out. Recently, the emphasis in many fields of study, especially in the use of metals in the electronic field, has been on high purity metals. With the advent of purifying the metals by zone refining, melting in vacuum or in controlled atmospheres, the gas content is often

* Ferrovac Iron—Crucible Steel Co., Syracuse, New York, U.S.A.

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only a few ppm. Therefore, it becomes imperative to investigate all sources of error.

McDonald, Fagel and Balis[18] admitted carbon monoxide gas in their study of the iron bath when applied to the determination of oxygen in zirconium. Beach and Guldner[22] carried out a comprehensive and systematic study of gas absorption by starting out with the carbon film followed by a superimposed metal film. All conditions were adjusted to simulate fusion analyses. The results show that hydrogen was lost to the carbon film. However, it was found that when a metal was fused in the graphite crucible, the metal vapour depositing over the carbon reduced the hydrogen loss by a factor of 2. Iron, platinum, platinum-titanium and germanium films, when exposed to carbon monoxide and nitrogen from 2 to 150 mm^3 sorbed less than 2 mm^3 of gas. Nickel was unusual, since the errors for carbon monoxide recovery were both positive and negative, especially when small amounts were added. Nitrogen and hydrogen losses were about the same as for the other metals. Aluminium and manganese sorbed so much carbon monoxide that fusion analyses of these metals would be prohibitive. Only by using extremely large bath:sample ratios would it be possible to analyse such metals. Certainly, it is recommended that similar work should be carried out on other metals, especially when the impurity level is only a few ppm.

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CONCLUSION

It is gratifying to note that most laboratories are providing for the analysis of gases in metals. Vacuum fusion offers the most widely used apparatus since it is capable of measuring oxygen, hydrogen and nitrogen in most metals. This method is currently the most sensitive.

Inert fusion offers an excellent means for the rapid determination of oxygen in metals, especially where the level is 50 ppm or more. Inert fusion has found wide application to the determination of oxygen in the refractory metals. The results are in good agreement with those obtained by vacuum fusion. One main advantage is that about 4 samples can be analysed per hr.

The conductimetric method for carbon is now widely used since a determination can be made in about 8 min. The sensitivity of the method can be changed by simply changing the concentration of the barium hydroxide.

The most satisfactory method for the determination of hydrogen in metals is by hot extraction. All samples are introduced to the analysis station through a vacuum lock. The analysis time is about 30 min per sample.

Since the current interest has been in high purity material, further research should be sponsored in exploring such methods as neutron activation, spectroscopy and isotope dilution to determine if these methods could be applied to metals having an impurity level below 10 ppm. Every effort should be made to encourage and support a programme for providing gas-metal standards of different impurity levels. Co-operative efforts of several gas-metal committees are working to achieve this goal.

Zusammenfassung—Eine Übersicht über die Bestimmung von Sauerstoff, Wasserstoff, Kohlenstoff und Stickstoff wird gegeben. Jüngste Entwicklung in Hinblick auf Apparate und Technik, soweit sie erhöhte Genauigkeit oder grössere Schnelligkeit erbrachten, werden besonders hervorgehoben. Schmelzen in inerter Gasatmosphäre wird behandelt, sowie Neuerungen, die die verwendeten Apparate verbessern und universeller anwendbar machen. Da viele Metalle Schmelzen oder Legieren erfordern, werden das Platinbad und die Platinschmelze besonders eingehend behandelt. Vorschläge für Verbesserungen und weitere Entwicklung werden gemacht, besonders für hochreine

Metalle und Fälle wo nur geringe Probenmengen zur Verfügung stehen. Es wird angeregt, Methoden zu entwickeln und zu untersuchen, die die Bestimmung von Stickstoff in Metallen ermöglichen.

Résumé—L'auteur passe en revue les méthodes de dosage de l'oxygène, de l'hydrogène, de l'azote et du carbone. Il discute les récents développements d'appareillage et de technique qui ont contribué à effectuer des analyses plus précises et plus rapides. La fusion dans un gaz inerte est passée en revue ainsi que les progrés récents qui ont contribué à faire de cet appareillage un instrument de contrôle très souple et excellent. Comme un grand nombre de métaux nécessite un bain ou un fondant pour former un alliage avec l'échantillon, l'auteur fait une revue critique des bains de platine, des fondants de platine et de l'injection intermittente de bains. Des recommandations sont faites pour des developpements ultérieurs des méthodes capables d'analyser des métaux de haute pureté contenant moins de 10 ppm., et ou la quantité d'échantillon est limitée. Aussi, de nouvelles méthodes ou techniques devràient être étudiées pour le dosage d'azote dans les métaux, particulièrement les métaux réfractaires et les alliages.

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THE PHOTOMETRIC DETERMINATION OF ZINC WITH XYLENOL ORANGE

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Summary—The use of Xylenol Orange as a reagent for the photometric determination of zinc is described. With this reagent, zinc forms a red complex at pH > 4, the optimal pH being 5·8–6·2. It was found that under these conditions only one complex, of molar ratio Zn:XO = 1:1, is formed. From Job's curve, the stability constant has been determined ($K \simeq 1{\cdot}4 \times 10^6$). In the region 0–100 μg of zinc/50 ml the Lambert-Beer law holds. This reaction has been applied to the determination of zinc in bronze after a prior separation with an ion-exchanger.

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XYLENOL Orange has been described by Körbl and Přibil[1,2] who found it to be an excellent complexometric indicator in an acidic medium. As a photometric reagent it has recently been used by Cheng for the determination of zirconium,[3] hafnium,[4] iron[5] and bismuth.[6] These determinations, when carried out in a relatively strongly acid medium, exhibit high selectivity. In spite of the fact that the reactions of other elements do not exhibit this selectivity in a weakly acid medium, the reaction of zinc has been studied, since there are not sufficient suitable reactions for the photometric determination of this element. In the light of the possibility of the separation of zinc from interfering elements using an ion-exchanger, the lower selectivity of the reaction is not a serious disadvantage.

EXPERIMENTAL

Reagents

Xylenol Orange (Lachema): 0·001*M* solution in 10 % ethanol.

Standard zinc solution: Prepared from zinc sulphate in such a way that 1 ml of the solution contained 100 or 10 μg of zinc. The actual strength was determined complexometrically.

Buffer solution: Prepared from 0·2*M* acetic acid and 0·2*M* sodium acetate.

The solutions of the other elements were prepared from salts of the highest possible purity, strengths being determined complexometrically.

Apparatus

All the measurements were made on a Pulfrich photometer with an Elpho adaptor. The absorption curve was obtained with a Beckman DU spectrophotometer. For the measurement of pH a Multoscope II pH-meter was used.

The effect of pH

Five-ml portions of standard zinc solution (50 μg) were pipetted into a series of 50-ml volumetric flasks, and 20 ml of buffer solutions of appropriate pH and 2 ml of 0·001*M* Xylenol Orange solution were added to each flask. The solutions were diluted to the mark with water. A similar series of solutions was prepared without the addition of zinc. The extinction was measured, using 2-cm cuvettes, a tungsten lamp and an S57 filter against water. The results obtained are shown in Fig. 1

The red complex of the reagent with zinc is formed at pH 4·0. The reagent alone, which is yellow at pH $\lesssim$ 5, turns to orange with an increase of pH, and at pH $>$ 7 has nearly the same colour as the zinc complex. The greatest difference of extinction

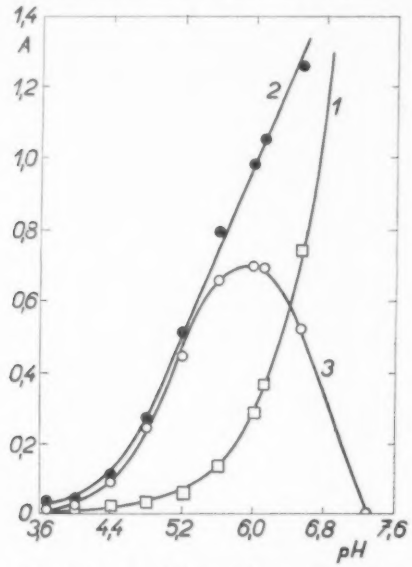

FIG. 1.—Dependence of the extinction of Xylenol Orange and its zinc complex on pH (574 mμ).
1—Xylenol Orange.
2—Xylenol Orange with addition of 50 μg of zinc.
3—Difference between curves 1 and 2.

is obtained at pH 5·8–6·2. This is obviously the optimum value for the determination of zinc, and it is necessary to remain within the given limits.

Absorption curves

The absorption curves of Xylenol Orange and its zinc complex at pH 6·0 $\pm$ 0·1 are presented in Fig. 2.

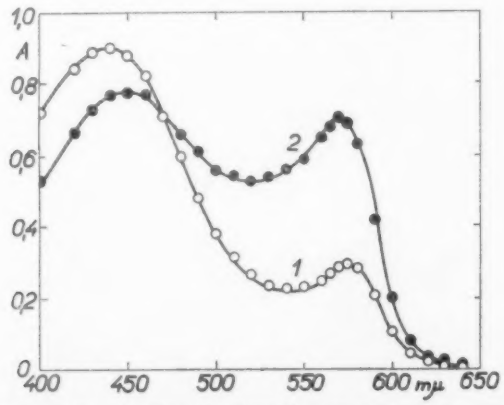

FIG. 2.—Dependence of the extinction of Xylenol Orange and its zinc complex on wavelength (pH 6·0 $\pm$ 0·1).
1—Xylenol Orange
2—Xylenol Orange with addition of 60 μg of zinc.

The reagent alone exhibits two maxima: a higher one at 440 mμ, and a lower one at 575 mμ. These maxima correspond to the yellow and red components of the colour of the solution.

The zinc complex (60 μg of zinc) exhibits a maximum at 570 mμ, a second maximum at 450 mμ corresponds to the yellow component of excess of reagent. For a low zinc content (10 μg) the maxima agree with the reagent alone.

The amount of Xylenol Orange

Portions of 6·5 ml of standard zinc solution (65 μg = 0·001 mole of zinc) were pipetted into a series of 50-ml volumetric flasks, followed by 10 ml of acetate buffer (pH 6) and from 0·2-ml to 5-ml amounts of 0·001*M* reagent solution. The solutions were diluted to the mark with water. A series of blank solutions (without the addition of zinc) were also prepared. The corresponding pairs of solutions were measured against each other, and the results are shown in Fig. 3.

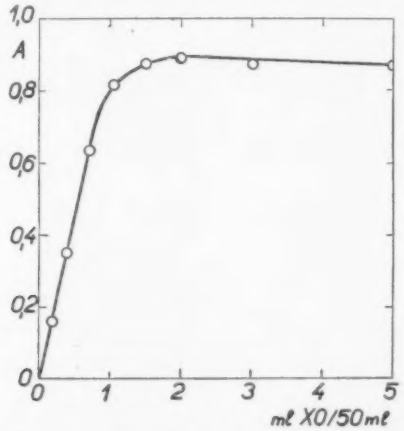

FIG. 3.—Dependence of the extinction on the amount of Xylenol Orange. (65 μg of zinc, pH 6·0 $\pm$ 0·1, 574 mμ.)

From this, it is obvious that for 65 μg of zinc about 2 ml of 0·001*M* reagent solution are sufficient. By extrapolation, the point of intersection obtained corresponds with a complex of the molar ratio Zn : XO = 1 : 1. This is further supported by applying Job's method (see later.)

Calibration curve

Portions of 0–10 ml of standard zinc solution (0–100 μg of zinc) were pipetted into a series of 50-ml volumetric flasks, 10 ml of buffer (pH 6) and 3 ml of 0·001*M* reagent solution were added and the solutions were diluted to the mark. The extinctions were measured under these conditions, and the curve is presented in Fig. 4.

This curve is in good agreement with the Lambert-Beer law throughout the full range of concentration used.

Composition of the complex and stability constant

Job's method of continuous variation was used to investigate the composition of the complex. The initial concentration of the zinc solution and the reagent was $5 \times 10^{-4}M$. The measurements were carried out at pH 6·0 for three wavelengths. The results are given in Fig. 5.

The curves exhibit maxima at the molar ratio Zn : XO = 1 : 1, confirming the formation of this complex alone under the given conditions. From curve 1 (Fig. 5)

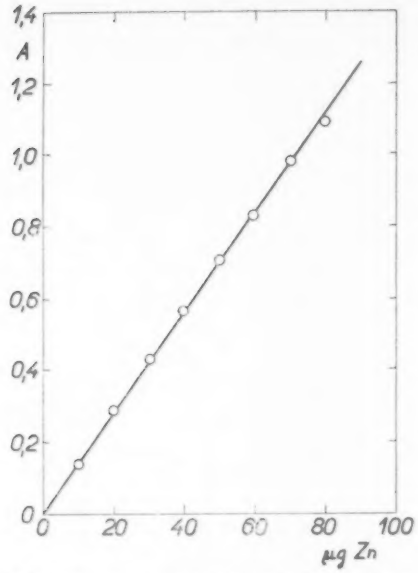

FIG. 4.—Calibration curve. (pH 6·0 ± 0·1, 574 mμ, 2-cm cuvettes.)

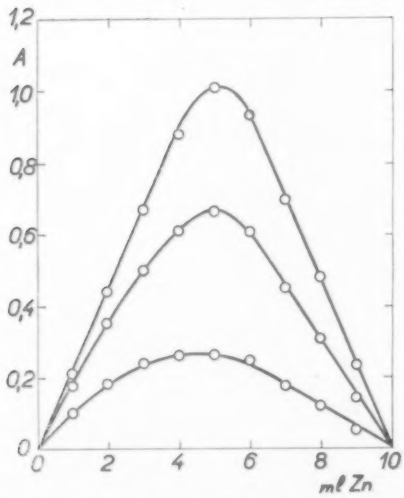

FIG. 5.—Job's curves for the zinc-Xylenol Orange complex (pH 6·0 ± 0·1).
Top—574 mμ: middle—530 mμ: bottom—492 mμ.

the approximate value of the stability constant of the complex has been determined as $k \simeq 1{\cdot}4 \times 10^6$. This is of the same order as the stability of the complex with hafnium.[4]

Determination of zinc in bronzes

The method has been applied to the determination of 0·01 — 0·50% of zinc in copper alloys (bronzes). For the separation of zinc from other elements a strongly basic ion-exchanger was used.*

* Strongly basic ion-exchanger (Research Institute of Synthetical Resins, Pardubice, Czechoslovakia.)

The sample is dissolved in nitric acid and evaporated to small volume. The solution is filtered into a volumetric flask and made to the mark with water. From a suitable aliquot of this solution, copper and lead are separated electrolytically. The solution is again transferred to a volumetric flask, and an aliquot corresponding to about 20–40 mg of the sample is evaporated to dryness. The residue is dissolved in 5 ml of 2N hydrochloric acid, and separated on a column of the ion-exchanger in the chloride form (5 ml, grain size 0·1–0·2 mm, rate of flow 1 ml/min). The column is washed with 50 ml of 2*N* hydrochloric acid, and zinc is eluted with 25 ml of 0·1*N* hydrochloric acid. The eluate is evaporated to dryness. The residue is dissolved in water and transferred to a 50-ml volumetric flask. The remainder of the procedure is as described for preparing the calibration curve. The extinction is measured against a blank solution which has been carried through the above procedure.

DISCUSSION

From the results obtained it is obvious that Xylenol Orange can be used for the comparatively selective photometric determination of zinc when suitable conditions are observed. The optimum value of the pH is 6·0 ± 0·1, at which value the greatest difference between the extinction of the zinc complex and that of the reagent is obtained. The value of pH mentioned is best achieved with an acetate buffer. A wavelength of about 570 mμ is the most suitable for measuring the extinction. The difference in extinction between the complex and the reagent is maximal in this wavelength region. The stability of the colour is stable under the given conditions for at least 3 hours.

A difficulty in the practical application of the method is its small selectivity if directly applied. Xylenol Orange, in a weakly acidic medium, reacts with a range of elements such as Cu, Al, Fe, Ni, Mn, Pb. All these elements can, however, be separated by electrolysis followed by the use of an ion-exchanger.

Preliminary experiments showed that at pH 6·0 the copper complex exhibits the same absorption maximum as that of zinc. The lead complex, under the same conditions, exhibits a maximum at about 530 mμ. At 575 mμ the extinction of the copper complex, under the same conditions, corresponds to about 56%, and of the lead complex to about 30% of the extinction measured for the zinc complex. Thus the determination of zinc in the presence of these metals suffers serious interference, even at the 10-μg level, and their separation is essential.

When using the method for the determination of zinc in bronzes at the 0·05% level, the standard deviation in 8 determinations was ±0·009%; at the 0·16% level of zinc, it was ±0·015%.

Acknowledgement—It is our pleasant duty to thank Mr. B. Kysil, SONP Kladno, for the measurement of the absorption curve.

Zusammenfassung—Eine photometrische Methode zur Bestimmung von Zink mit Xylenolorange wird beschrieben. Der rote Komplex wird oberhalb pH 4 geformt, der beste pH-Bereich ist 5·8–6·2. Unter den beschriebenen Bedingungen wird ein 1:1 Komplex geformt. Aus einer Job-Kurve wurde die Stabilitätskonstante des Komplexes zu etwa $1{\cdot}4 \times 10^6$ bestimmt. Im Bereich 0–100 μg Zn/50 ml ist Beer's Gesetz erfüllt. Die Methode wurde zur Bestimmung von Zink in Bronzen herangezogen. Eine Trennung unter Verwendung eines Anionenaustauschers geht dem Photometrieren voraus.

Résumé—Les auteurs décrivent l'utilisation de xylénol orange comme réactif pour le dosage photométrique du zinc. Le zinc forme un complexe rouge à pH > 4. La condition la meilleure pour le dosage est à pH 5,8–6,2. Dans les conditions décrites, un complexe se forme, de rapport molaire Zn/XO = 1/1. D'après la courbe de Job, la constante de stabilité a été déterminée: $K \sim 1{,}4 \cdot 10^{-6}$. Dans le domaine 0–100 μg de Zn pour 50 ml, la loi de Lambert-Beer est suivie. La réaction a été appliquée au dosage du zinc dans le bronze après une séparation préliminaire sur un échangeur d'ions.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—VI*

THE DETERMINATION OF TANTALUM AND NIOBIUM

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Summary—A method is described for the determination of tantalum and niobium in beryllium or beryllium oxide. These two elements are precipitated with cupferron, using zirconium as a collector. A further separation from other elements is obtained by passing a mixed chloride-fluoride solution through a column containing a strongly basic anion-exchange resin. Niobium and tantalum are selectively eluted from the column and finally determined spectrophotometrically, niobium with hydroquinone and tantalum with pyrogallol. For niobium, the method is accurate to ±5% or 10 μg, whichever is greater, and for tantalum it is accurate to ±10% or 30 μg, whichever is greater. No interference was caused by the presence of 10-mg amounts of 68 elements.

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INTRODUCTION

A METHOD for the determination of niobium and tantalum is presented which is specific within the limits investigated. No interference was caused by 10-mg amounts of 68 elements.

The method is based on the precipitation of niobium and tantalum from a mixed hydrochloric–sulphuric acid solution with cupferron using zirconium as a collector. A hydrochloric–hydrofluoric acid solution, containing the niobium and tantalum and other elements quantitatively or partly precipitated with cupferron (antimony, bismuth, copper, gallium, hafnium, iron, molybdenum, palladium, tin, titanium, vanadium, tungsten, and zirconium), is passed through a column containing Dowex-1X8 anion-exchange resin. Niobium and tantalum and a portion of the tin are retained, all other elements passing unadsorbed into the eluate. Niobium is subsequently eluted with a mixture of hydrofluoric acid and ammonium chloride. Tantalum is eluted with a mixture of ammonium fluoride and ammonium chloride. The ion-exchange separation of niobium and tantalum, from each other and from other elements, is a modification of work published by Krause and Moore[1] and Hague *et al.*[2] The two elements are again precipitated with cupferron using zirconium as a collector. Niobium is finally determined spectrophotometrically with hydroquinone in a concentrated sulphuric acid medium.[3] The absorbance, measured at 395 or 490 mμ, is a linear function of the niobium concentration, at least from 0 to 4 μg of niobium per ml, and is stable for at least 24 hr. Tantalum is determined spectrophotometrically with pyrogallol in a mixed ammonium citrate-ammonium oxalate-sulphuric acid medium.[3] The absorbance, measured at 398 or 420 mμ, is a linear function of the tantalum concentration, at least from 0 to 12 μg of tantalum per ml, and is stable for at least 24 hr.

* Part V, see *Talanta*, 1961, **8**, 104.

EXPERIMENTAL

Apparatus

Beckman DU and Cary Model 14 spectrophotometers with 5-cm cells.

Ion-exchange columns: Polyethylene or polystyrene, 1-cm internal diameter, 15-cm long, containing 10 cm of Dowex-1, 200–400 mesh, 8% crosslinkage.

Reagents

Distilled water used throughout.

Standard niobium solution: Fuse 0·1431 g of niobium pentoxide with 5 g of potassium bisulphate. Dissolve the fused mass with 100 ml of 4% ammonium oxalate and dilute the clear solution to 1 litre. Dilute this solution to obtain a solution containing 10 μg of niobium per ml.

Standard tantalum solution: Fuse 0·1221 g of tantalum pentoxide with 5 g of potassium bisulphate. Dissolve the fused mass with 100 ml of ammonium citrate-ammonium oxalate solution (see below) and dilute the clear solution to 1 litre. Dilute this solution to obtain a solution containing 10 μg of tantalum per ml.

Zirconium sulphate solution: Dissolve 0·1 g of zirconium metal in dilute hydrofluoric acid, add 5 ml of sulphuric acid, evaporate to sulphur trioxide fumes and dilute to 100 ml. One ml contains 1 mg of zirconium.

Boric acid

Hydrofluoric acid, 29*M*.

Hydrochloric acid, 12*M*, 6*M* and 1*M*.

Sulphuric acid, 18*M*, 9*M*, 6*M* and 0·45*M*.

Nitric acid, 16*M*.

Cupferron 6% (w/v) aqueous solution, freshly prepared.

Potassium bisulphate

Ammonium hydroxide, 15*M*.

Sodium bisulphate

Eluent No. 1: Dilute 250 ml of hydrochloric acid and 200 ml of hydrofluoric acid to 1 litre with water.

Eluent No. 2: Dissolve 140 g of ammonium chloride in water, add 40 ml of hydrofluoric acid and dilute to 1 litre.

Eluent No. 3: Adjust the pH of Eluent No. 2 with ammonium hydroxide to 5·7 $\pm$ 0·2.

Hydrogen peroxide, 30%.

Hydroquinone solution: Dissolve 50 g of hydroquinone in 18*M* sulphuric acid and dilute to 1 litre with the same acid. Prepare fresh as needed.

Tin^{II} chloride solution: Dissolve 10 g of tin^{II} chloride in 40 ml of 6*M* hydrochloric acid and dilute to 100 ml with the same acid.

Ammonium citrate-ammonium oxalate mixture: Dissolve 3 g of ammonium citrate and 3 g of ammonium oxalate in 100 ml of 0·45*M* sulphuric acid.

Ammonium oxalate: 4% (w/v) aqueous solution.

Pyrogallol: Some commercially available material results in a cloudy solution when the tantalum complex is formed. It is quite important that the solution whose absorbance is to be measured is clear.

Procedure

Transfer a sample containing 20 to 200 μg of niobium and/or 25 to 300 μg of tantalum to a 600-ml beaker. Dissolve beryllium oxide in hot 6 *M* sulphuric acid (25 ml for 1 g of beryllium oxide, 50 ml for 3 g). Dissolve beryllium metal by suspending the sample in water and gradually adding hydrochloric acid (10 ml for a 1-g sample). When the reaction ceases, add, if necessary, a few drops of 30% hydrogen peroxide to dissolve any remaining particles of unoxidised metal. Heat to destroy the excess peroxide. Inasmuch as niobium and tantalum are to be precipitated and ignited, they need not be completely dissolved by this treatment. If the sample was dissolved in 6*M* sulphuric acid, add 10 ml of hydrochloric acid. If the sample was dissolved in hydrochloric acid, add 25 ml of 6*M* sulphuric acid. Dilute to about 150 ml.

Add 10 ml of zirconium sulphate solution and a little filter pulp. Cool the sample solution, the 6% cupferron solution, and a wash solution of 1*M* hydrochloric acid containing a little cupferron to

10–15°. Add 15 ml of cupferron solution.[4] Filter, using Whatman No. 40 filter paper, and wash the precipitate 10 to 15 times with the wash solution. Ignite the precipitate in a platinum crucible and fuse the residue in about 2 g of sodium bisulphate. Sodium bisulphate is used in this case rather than the potassium salt because of the tendency for potassium fluotantalate to precipitate. Dissolve the melt in a polyethylene beaker with 50 ml of Eluent No. 1. Pass this solution through the anion-exchange column and wash with 50 ml of the same eluent, discarding the eluate. Pass 60 ml of Eluent No. 2 through the column. Collect the eluate, containing the niobium and possibly a small amount of tin, in a polyethylene beaker. Replace this beaker with another polyethylene beaker and elute tantalum with 60 ml of Eluent No. 3.

To each of the two eluates add 8 g of boric acid dissolved in about 100 ml of hot water. Add 20 ml of 12*M* hydrochloric acid and transfer the solutions to 400-ml beakers. Dilute to approximately 250 ml. Add 10 ml of zirconium sulphate solution, followed by some filter pulp and 15 ml of cupferron solution. Perform the precipitations below 15° as before. Filter and wash the precipitate 15 times with 1*M* hydrochloric acid containing a little cupferron. Proceed with the treatment of the niobium and tantalum precipitates as follows.

Niobium: Ignite the precipitate in a platinum crucible. Fuse the residue in 1 g of potassium bisulphate and dissolve the melt with 50 ml of 4% ammonium oxalate solution.

Transfer the solution or an aliquot containing about 200 μg of niobium to a 100-ml beaker. Add 10 ml of 9*M* sulphuric acid. If an aliquot is taken, add sufficient potassium bisulphate to provide 1 g of this salt. Add 5 ml of 16*M* nitric acid and 3 ml of 12*M* hydrochloric acid. Evaporate the solution to sulphur trioxide fumes. Add 2 or 3 drops of hydrogen peroxide and 1 ml of water and again evaporate to fumes. Repeat the addition of hydrogen peroxide until there is no further evidence of organic material when the sample is evaporated to sulphur trioxide fumes. Wash down the sides of the beaker with water and again evaporate to fumes. Repeat the water rinse and evaporation step several times. It is essential that organic material is completely destroyed and that nitric acid is completely removed.

Cool, add 1 drop of tin[II] chloride solution, 25 ml of hydroquinone solution and transfer to a 50-ml volumetric flask, using hydroquinone solution for washing purposes. Dilute to the mark with hydroquinone solution and mix. Allow to stand for 10 min and measure the absorbance in 5-cm cells at 490 mμ using a reagent blank carried through the entire procedure as a reference. Determine the niobium concentration by reference to a calibration curve obtained by treating aliquots of the standard niobium solution as described in the previous paragraph. A blank and standard should be carried through the entire procedure.

Tantalum: Ignite the cupferron precipitate in a Vycor or quartz crucible. A platinum crucible is not used here because of the interference of platinum in the determination of tantalum with pyrogallol.[5] Fuse the residue with 0·5 g of potassium bisulphate and dissolve the melt with 15 ml of ammonium citrate-ammonium oxalate solution. Transfer the solution, or an aliquot containing about 300 μg of tantalum, to a 25-ml volumetric flask. If an aliquot is taken, add sufficient potassium bisulphate to provide 0·5 g of the salt. Add 3·0 $\pm$ 0·1 g of pyrogallol and swirl until a clear solution results. Dilute to the mark with ammonium citrate-ammonium oxalate solution. Mix, allow to stand for 10 min, and measure the absorbance in 5-cm cells at 398 or 420 mμ depending upon the instrumentation available, using a reagent blank carried through all steps of the procedure in the reference cell. Determine the tantalum concentration by reference to a calibration curve prepared by adding pyrogallol to aliquots of the standard tantalum solution and diluting to 25 ml with ammonium citrate-ammonium oxalate solution. A blank and standard should be carried through the entire procedure.

DISCUSSION AND RESULTS

Measurement of the niobium-hydroquinone complex

The absorbance of the niobium-hydroquinone complex, although a maximum at 395 mμ, is usually measured at 490 mμ, presumably because of (*a*) the lack of adequate instrumentation, (*b*) the high blank at 395 mμ (when measured in 5-cm cells using sulphuric acid as a reference, the blank is about 0·6 at 395 mμ compared to about 0·3 at 490 mμ), and (*c*) the fact that niobium seriously interferes at 395 mμ whereas little interference is apparent when the absorbance is measured at 490 mμ. The absorbance,

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measured at either wavelength, is a linear function of the niobium concentration, at least from 0 to 4 μg of niobium per ml, and is constant for at least 24 hr. The absorbance of a solution containing 2 μg of niobium per ml, in 5-cm cells, is approximately 0·5 at 490 mμ and 1·1 at 395 mμ (using a reagent blank in the reference cell). A two-fold increase in sensitivity may be obtained by making absorbance measurements using 10-cm cells. Using the procedure described for the formation of the niobium-hydroquinone complex, the absorbance of 1 mg of tantalum is equivalent to approximately 5 μg of niobium at 490 mμ and approximately 105 μg at 395 mμ.

Measurement of the tantalum-pyrogallol complex

The absorbance of the tantalum-pyrogallol complex is a maximum at 398 mμ. However, the absorbance of the complex is frequently measured at 420 mμ, presumably because of the lack of adequate instrumentation. The absorbance measured at either wavelength, is a linear function of the tantalum concentration, at least from 0 to 12 μg of tantalum per ml, and is constant for at least 24 hr. The absorbance of a solution containing 12 μg of tantalum per ml, using 5-cm cells, is approximately 0·9 at 398 mμ and 0·8 at 420 mμ. The absorbance is unaffected by the use of 1·5 g of potassium bisulphate rather than the 0·5 g called for in the procedure. The amount of pyrogallol should be controlled at 3·0 $\pm$ 0·1 g. The use of greater or less pyrogallol causes a change in absorbance amounting to about 10% per g between 2 and 4 g. Although an increase in the amount of pyrogallol used would result in an increased absorbance, the coloured solution becomes turbid when the amount is slightly greater than 4 g.

Using the procedure described for the formation of the tantalum-pyrogallol complex, the absorbance of 1 mg of niobium is equivalent to that of 4 μg of tantalum, at both 398 and 420 mμ.

Effect of other elements

In testing the effect of other elements on the determination of niobium and tantalum by the above procedure, the elements were added to a solution containing the appropriate amounts of beryllium sulphate, sulphuric and hydrochloric acids, before the precipitation with cupferron preceding the ion-exchange separation.

No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, As^{III}, Ba, Bi, B, Br, Cd, Ca, Ce^{IV}, Cs, Cr^{III}, Co, Cu^{II}, Dy, Er, Eu, F, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Hg^{II}, Mo^{VI}, Nd, Ni, Nb (for Ta determination), Pd^{IV}, P(as PO_4^{3-}), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Na, Sr, Ta(for Nb determination), Te^{IV}, Tb, Tl^{I}, Th, Tm, Sn^{IV}, Ti^{IV}, W^{VI}, U^{VI}, V^{V}, Yb, Y, Zn or Zr.

It should be noted that the preliminary precipitation with cupferron separates niobium and tantalum from all but antimony, bismuth, copper, gallium, hafnium, iron, molybdenum, palladium, tin, titanium, vanadium, tungsten and zirconium.

The subsequent anion-exchange step provides two solutions. One contains niobium and part of the tin originally present in the sample, the other contains only tantalum. Tin does not interfere with the niobium determination, being used as a reagent in the final spectrophotometric determination with hydroquinone.

Application of the method

A 10-g sample of beryllium oxide analysed for niobium and tantalum using this procedure was found to contain less than 1 ppm of niobium and less than 3 ppm of

TABLE I. RECOVERY OF NIOBIUM AND TANTALUM ADDED TO BERYLLIUM OXIDE

BeO, *g*	Nb added, *μg*	Nb found, *μg*	Ta added, *μg*	Ta found, *μg*
2	15	21·0	—	—
5	50	54·2	—	—
5	100	97·3	—	—
5	225	218·0	200	208·3
5	200	—	500	519·3
5	—	—	50	43·0
5	—	—	150	158·9
5	—	—	250	245·3
5	—	—	400	382·7
5	200	—	400	390·2
5	2000	—	250	254·4
5	250	247·6	2000	—

tantalum. The recovery of niobium and tantalum added to this sample of beryllium oxide is shown in Table I.

No niobium or tantalum was found in 3-g portions of New Brunswick Laboratory standard samples of beryllium metal (85, 86, 87, 88) and beryllium oxide (72–1, 72–2, 72–3, 72–4, 72–5), indicating the concentration of niobium in these samples to be less than 3·3 ppm and that of tantalum less than 10 ppm.

Zusammenfassung—Eine Methode zur Bestimmung von Tantal und Niob in Beryllium und dessen Oxyd wird beschrieben. Die beiden Elemente werden mittels Cupferron gefällt unter Verwendung von Zirkonium als Collector. Eine Trennung von weiteren Ionen wird erzielt, indem man die Lösung, die Fluss- und Salzsäure enthält, durch einen starken Anionanaustauscher schickt. Niob und Tantal werden selktiv eluiert und schliesslich photometrisch bestimmt; Niob mit Hydrochinon und Tantal mit Pyrogallol. Die Methode ist genau auf 5% oder 10 μg Niob und 10% oder 30 μg Tantal, was immer der grössere Wert ist. Keine Störung wird versucht durch Anwesenheit von 10-mg Mengen von 68 geprüften Fremdelementen.

Résumé—Les auteurs décrivent une méthode de dosage du tantale et du niobium dans le béryllium ou l'oxyde de béryllium. Ces deux éléments sont précipités par du cupferron, le zirconium étant utilisé comme collecteur. Une séparation ultérieure des autres éléments est réalisée en faisant passer une solution de chlorure et fluorure mélangés sur une colonne contenant une résine échangeuse d'anions fortement basique. Le niobium et le tantale sont élués sélectivement et sont dosés finalement par spectrophotomètrie, le niobium avec de l'hydroquinone et le tantale avec du pyrogallol. Pour le niobium, la méthode est précise à ±5% ou 10 μg et pour le tantale à ±10% ou 30 μg. La présence de quantités de l'ordre de 10 mg de 68 éléments ne gêne pas le dosage.

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THE ANION-EXCHANGE SEPARATION OF TIN, ANTIMONY, LEAD AND COPPER

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Summary—The selective adsorption of anionic complexes of tin, antimony, lead and copper on an anion-exchange resin is used for their quantitative separation from each other. The method is subsequently adapted to the analysis of alloys.

INTRODUCTION

THE widespread employment of alloys containing varying amounts of tin, lead, copper and antimony, together with the tediousness of established methods for their analysis, have prompted the search for a stepwise anion-exchange separation of these metals.

Conditions for the adsorption on anion-exchange resins, from various media, have been determined for most of the above metals[1] and single components have also been separated from others,[2,3] but no complete stepwise separation of this metal system, allowing the successive determination of its components, has been described.

DISCUSSION

The separation of metals on anion-exchange resins is based on the selective adsorption of their anionic complexes on the resin, this being a function of the nature of the complex-forming ligand, the composition of the medium employed, *etc.* Adsorption curves from a base electrolyte of the type HL usually exhibit maxima, due to the formation, at high acidities, of an uncharged species, $H_s\ ML_n$. This complex does not, to any appreciable extent, enter the resin; its formation, therefore, is accompanied by a decrease in the concentration of metal in the resin phase. The heights and relative positions of these maxima vary from metal to metal, according to the stability of the metal-ligand complexes, their dimensions, *etc.*

From published adsorption curves[1] it appears that many elements may be separated, singly or in groups, employing hydrochloric acid and an anion-exchange resin; the co-employment of other eluents greatly widens the applicability of the method.

It was decided to use these curves as a starting point, rather than employ the recent half-theoretical approach of building adsorption curves,[4] since the presence of numerous adverse factors, such as probable side reactions and the un-ideal systems incurred, made this appear impracticable.

From a consideration of data published by Kraus and Nelson[1] for adsorption on Dowex-1 resin, several possibilities of separation for the Sn-Sb-Cu-Pb system seemed feasible. Table 1 contains pertinent distribution coefficient data for varying concentrations of hydrochloric acid, while similar data for 1*N* hydrofluoric acid, in

the presence of varying concentrations of hydrochloric acid, are summarised in Table II.

TABLE I.—ADSORPTION OF Sn^{IV}, Sb^{V}, Sb^{III}, Cu^{II} AND Pb^{II} FROM HYDROCHLORIC ACID
(D = DISTRIBUTION COEFFICIENT)

HCl, *N*	12	7	2·4	1·5
log D:				
Sn^{IV}	3·3	2	3	2·8
Sb^{V}	5·4	4·8	1·7	0
Sb^{III}	1·2	2	2	3·3
Cu^{II}	1	1	0	0
Pb^{II}	0	0	1	1·1

TABLE II.—ADSORPTION OF Sn^{IV}, Sb^{V} AND Sb^{III} FROM MIXTURES OF HYDROCHLORIC ACID AND 1*N* HYDROFLUORIC ACID
(D = DISTRIBUTION COEFFICIENT)

1*N* HF—HCl; HCl, *N*	0·3	1	6
log D:			
Sn^{IV}	1·8	1	3
Sb^{V}	2·8	2	2·5
Sb^{III}	0·3	1	2

Because of the similarity of the resins, it seemed permissible to employ these data as starting points for a separation employing Amberlite IRA-400. This was borne out by the similarity of adsorption data for copper, obtained experimentally on both resins. The proposed sequence of elution steps, based on these data, is summarised in Fig. 1;

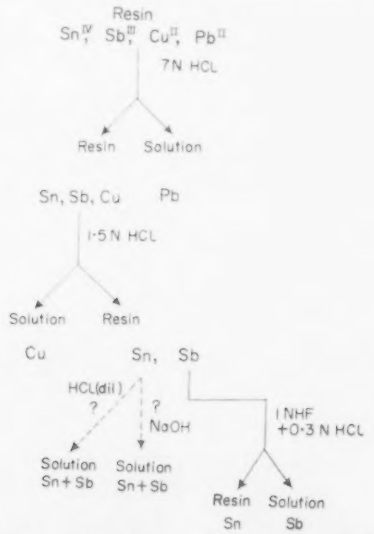

FIG. 1.—Scheme for the successive elution of Pb^{II}, Cu^{II}, Sb^{III} and Sn^{IV}.

for each successive elution step, eluents were chosen in which D for the element to be eluted was low and that of the others, to be retained in the column, high.

Column length, size of the resin particles and minimum volume of eluent necessary for each quantitative elution were computed theoretically,[5] and found suitable for the practical carrying out of the separation. The sample size chosen initially was small (*ca.* 1 mg for each metal), with a view to exploiting fully the speed and convenience of micro methods. Subsequent considerations limited the sample size further, the final method being applicable to samples containing up to 400μg of each metal. It was found that the precision obtainable was limited chiefly by the methods employed for the determination of the single components ($\pm 1\%$ maximum relative error) and not by the efficiency of the separation, which was better than this error limit.

Following the theoretical computations, the minimum volume of eluent necessary for the quantitative elution of 1 mg of each element was determined experimentally. The amount of elution of each element, as caused by the passage, through the column, of the eluents employed for the elements eluted previously, was also determined. The data of the elution curves obtained are condensed in Fig. 2. Inspection of this figure might indicate the feasibility of a successive separation of the four elements, based on the elution curves of the single metals. An experimental attempt to separate the elements, by passing volumes of eluents sufficient for their elution when present singly,

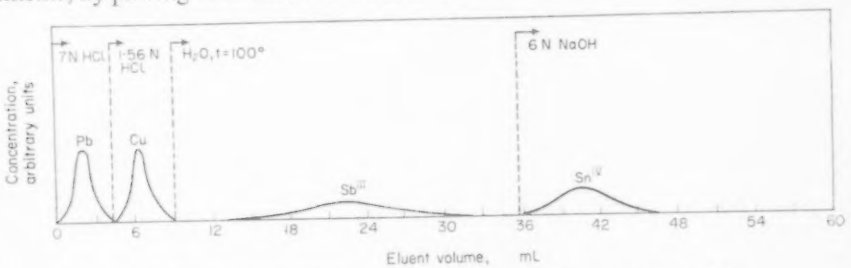

FIG. 2.—Elution curves for Pb^{II}, Cu^{II}, Sb^{III} and Sn^{IV} (present singly).

was, however, unsuccessful; as may be seen from Table III, only tin was eluted quantitatively; antimony remained in the column, while the elution of copper and lead was incomplete.

TABLE III.—ATTEMPTED SEPARATION OF A MIXTURE OF Sn^{IV}, Sb^{III}, Cu^{II} and Pb^{II}

Element	Eluent employed	Eluent volume, *ml*	Element in mixture, *mg*	Element eluted, *mg*	% eluted
Pb	7*N* HCl	4·0	0·500	0·150	30
Cu	1·56*N* HCl	4·0	0·500	0·389	78
Sb	H_2O at 100°	25·0	0·500	0	0
Sn	6*N* NaOH	10·0	1·000	0·995	100

It is apparent that in the presence of more than one element and as a result of their mutual interaction, the elution curves are displaced in the direction of larger eluent volumes required for quantitative separation. The extent of this displacement was determined experimentally; the results are given, in Fig. 3 for the elution of lead, in Figs. 4 and 5 for the elution of copper, and condensed in Fig. 6. As is apparent

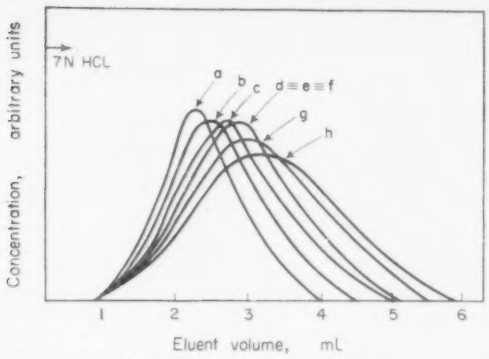

FIG. 3.—Elution curves for Pb^{II} from columns loaded with:
a. 0·2 mg of Pb^{II};
b. 0·2 mg of Pb^{II}, 1 mg of Cu^{II};
c. 0·2 mg of Pb^{II}, 1 mg of Cu^{II}, 1 mg of Sb^{III};
d. 0·2 mg of Pb^{II}, 1 mg of Cu^{II}, 1 mg of Sb^{III}, 0·4 mg of Sn^{IV};
e. 0·05 mg of Pb^{II}, 0·4 mg of Sn^{IV};
f. 0·05 mg of Pb^{II}, 0·5 mg of Sn^{IV};
g. 0·4 mg of Pb^{II}, 0·4 mg of Sn^{IV};
h. 0·05 mg of Pb^{II}, 2 mg of Sn^{IV}.

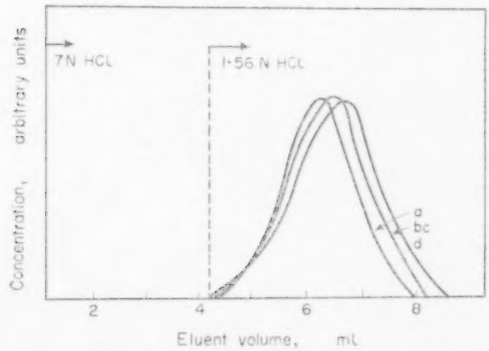

FIG. 4.—Elution curves for Cu^{II} from columns loaded with:
a. 1 mg of Cu^{II};
b. 1 mg of Cu^{II}, 0·2 mg of Pb^{II};
c. 1 mg of Cu^{II}, 0·2 mg of Pb^{II}, 1 mg of Sb^{III};
d. 1 mg of Cu^{II}, 0·2 mg of Pb^{II}, 1 mg of Sb^{III}, 0·4 mg of Sn^{IV}.

from Fig. 6 the efficiency of the separation can be upheld only by severely limiting the amount of tin present in the sample mixture, the upper limit being 400μg (see Fig. 6c; at this concentration of tin, there is minimum overlapping).

The elution of antimony, employing boiling water as eluent, is seriously disturbed by the presence of tin. Even 6*N* sodium hydroxide solution, which should elute both tin and antimony simultaneously, elutes tin quantitatively and does not elute antimony, which remains in the column and is not eluted by either hot water or 6*N* sodium hydroxide even after the tin has been removed quantitatively. No adequate explanation of this surprising retention of antimony has been found; it might be supposed that it is due to the formation, in the presence of tin, in sodium hydroxide solution or water, of some antimony compound which is tenaciously held by the resin.

As may be seen from Table II, a solution 0·3*N* in hydrochloric acid and 1*N* in hydrofluoric acid should elute antimony, leaving tin in the column. The tin may

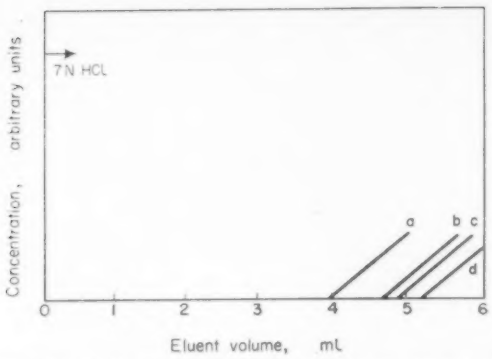

FIG. 5.—Elution curves for Cu^{II} from columns loaded with:
a. 1 mg of Cu^{II};
b. 1 mg of Cu^{II}, 0·4 mg of Sn^{IV};
c. 1 mg of Cu^{II}, 0·5 mg of Sn^{IV};
d. 1 mg of Cu^{II}, 2 mg of Sn^{IV}.

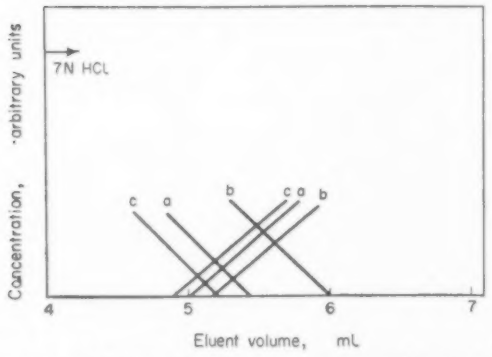

FIG. 6.—Overlapping of Pb^{II} and Cu^{II} elution curves, for varying amounts of Sn^{IV} present:
a. Condensation of data presented in Fig. 3f and Fig. 5c;
b. Condensation of data presented in Fig. 3h and Fig. 5d;
c. Condensation of data presented in Fig. 3e and Fig. 5b.

subsequently be eluted with 6*N* sodium hydroxide solution. The pertinent elution curves for 1 mg of each element were experimentally determined and are given in Figs. 7 and 8. The use of hydrofluoric acid demands the employment of corrosion-proof apparatus, the construction of which is described below (Fig. 9).

The separation of the four elements is feasible, as may be seen from Fig. 10 which contains the condensed facts of Figs. 3b, 4d, 5b, 7 and 8. Synthetic mixtures of varying proportions of the constituents were absorbed on the resin and the metals eluted successively by passing 5·2 ml of 7*N* hydrochloric acid for the lead, 5·2 ml of 1·56*N* hydrochloric acid for the copper, 7·7 ml of 1*N* hydrofluoric acid 1*N* in hydrochloric acid for the antimony and, finally, 10 ml of 6*N* sodium hydroxide solution for the tin. Each metal was determined in its eluate by methods specified in the experimental part of this paper. Blank determinations were carried out in each case, but were found significant for tin only, where they were properly deducted. The results obtained are given in Table IV.

The method was adapted to the analysis of tin- and lead-base alloys, which were dissolved in concentrated hydrochloric acid and either hydrogen peroxide or bromine

TABLE IV.—THE SEPARATION AND DETERMINATION OF Sn^{IV}, Sb^{III}, Cu^{II} AND Pb^{II} FROM THEIR MIXTURES

Metal content of sample, μg				Metal recovery after separation, μg							
Pb	Cu	Sb	Sn	Pb	Relative error, %	Cu	Relative error, %	Sb	Relative error, %	Sn	Relative error, %
		40·0	400·0					40·3	+0·3	397·0	−0·8
200·0			400·0	198·0	−1·0					406·0	+1·3
400·0		40·0		396·0	−1·0			39·7	−0·8		
40·0		40·0	400·0	39·5	−1·2			39·7	−0·8	395·0	−1·2
100·0	60·0	40·0	400·0	98·9	−1·1	59·0	−2·0	39·5	−1·2	397·0	−0·8

water or potassium chlorate, the solution obtained containing $copper^{II}$, $lead^{II}$, $antimony^{V}$ and tin^{IV}, hydrochloric acid and excess oxidising agent. Antimony may be reduced by various reagents such as sodium sulphite,[6] tin^{II} chloride,[7] $chromium^{II}$

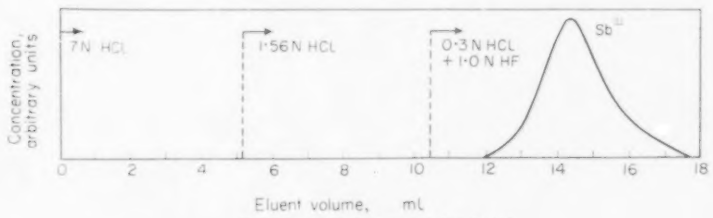

FIG. 7.—Elution curve for Sb^{III}.

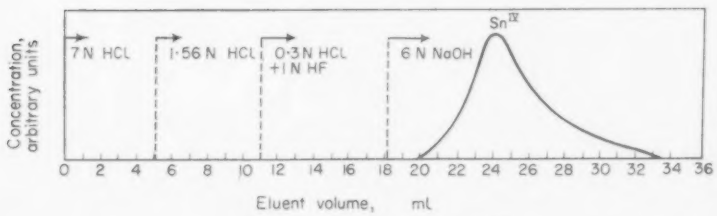
Concentration, arbitrary units
7 N HCl
1·56 N HCl
0·3 N HCl + 1 N HF
6 N NaOH
Sn(IV)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36
Eluent volume, ml

FIG. 8.—Elution curve for Sn^{IV}.

chloride,[8] $titanium^{III}$ chloride[9] or mercury metal.[10] It was considered inadvisable to introduce new cations, or anions which might complex the metals, into the system; hydrogen peroxide was, therefore, employed as oxidising agent and sodium sulphite as reducing agent. After reduction, the solution is ready for adsorption on the resin column, and elution by the method evolved. Table V contains the analysis of the alloys employed to test the method (according to A.S.T.M. methods), together with representative results obtained by the proposed procedure.

As may be seen, good results (±2% maximum relative error) may be obtained with this method; in view of the speed with which an analysis can be carried out (four parallel analyses may be completed in 2 hr) this seems satisfactory. The percentage composition of the alloys to which this method is applicable may vary considerably.

TABLE V.—ANALYSIS OF TIN- AND LEAD-BASE ALLOYS*

Analysis of alloy, %				Experimental results by proposed procedure, %					
Pb	Cu	Sb	Sn	Pb	Relative error	Sb	Relative error	Sn	Relative error
36·5			63·6	36·1	−1·1			63·0	−0·9
		6·22	93·8			6·16	−1·0	93·0	−0·9
94·7		5·00		93·2	−1·5	4·96	−0·9		
50·4	0·92	7·40	42·1	49·8	−1·3	7·34	−0·8	41·7	−1·0

* Copper was not determined after its separation; the amount present in the standard alloys available was too low for satisfactory determination by the spectrophotometric method employed.

EXPERIMENTAL

Apparatus

Polarographic determinations were carried out with a Type E Leeds Northrup Electro-Chemograph, spectrophotometric measurements with a Unicam SP 500-spectrophotometer, and potentiometric titrations with a Fisher Titrimeter.

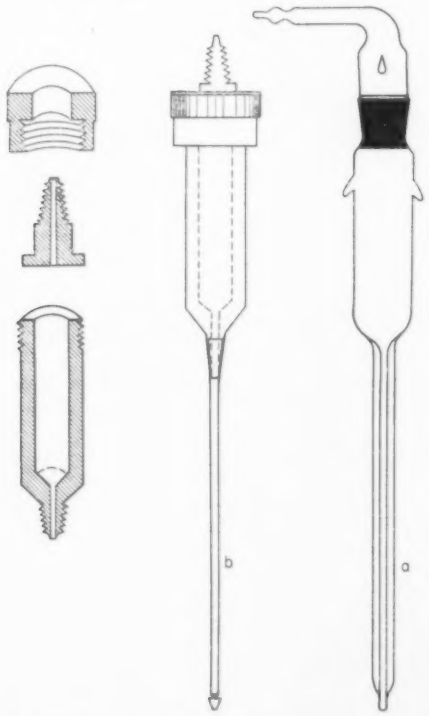

FIG. 9.—Construction details of columns employed.

Adsorption columns: The anion-exchange resin employed was 100–140 mesh Amberlite IRA-400, washed and decanted. The columns employed were 200 mm long, with an internal diameter of 3 mm. The eluents were passed through the column at the rate of 3 ml per min. Two kinds of columns were used in this work (Fig. 9): one constructed from glass only (Fig. 9a) and the other made of Plexiglass and Tygon tubing (Fig. 9b). The upper part of the latter column contains three Plexiglass parts; a section of 0·3-mm internal diameter and 200 mm long Tygon tubing is attached; this contains a small

conus of hard plastic material at its end, to serve as a support for some thin Plexiglass shavings on which the resin filling rests. Four such columns are connected, by means of individual pressure taps and a manifold, to a pressure source, such as an oxygen or nitrogen gas container. This arrangement allows the regulation of pressure for each column separately, without affecting the other three. After passing 4 ml of 7*N* hydrochloric acid through each column, the apparatus is ready for use.

Reagents

Standard copper, antimony tin and lead chloride stock solutions: Prepared by dissolving appropriate amounts of the pure metals in mixtures of hydrochloric acid and hydrogen peroxide, removing excess peroxide by boiling and making up to volume with hydrochloric acid (antimony was reduced to the tervalent state by adding small amounts of sodium sulphite to the solution and boiling, before the final dilution). From these, by appropriate dilution with 1:1 hydrochloric acid, the solutions employed in the experiments described, containing the single metal ions or their mixtures, were prepared.

Standard potassium bromate solution: Prepared by dissolving the pure, dried salt in water and checked against the standard antimony^{III} solution.

All other reagents were of reagent grade.

Procedures

The methods employed for the determination of the single components (after collection of the pertinent eluate fraction) are:

1. Lead was determined polarographically, a method based on the reduction of plumbite ion in 1*N* sodium hydroxide solution being employed.[11] The lowest limit for this determination was 10 mg of lead per litre, within the limits of error allowed.

2. Antimony was determined by potentiometric titration with potassium bromate.[12] This method gave rapid and accurate results, provided the oxide film formed on the platinum electrode[13,14] was removed by immersing the electrode for 15 min in a reducing solution (0·01*M* iron^{II} sulphate, 0·05*M* in sulphuric acid) after each titration. The hydrofluoric acid present in the eluate slowly attacks the glass parts of the electrodes, making their replacement advisable after *ca.* 50 titrations. One mg of antimony per litre could still be easily determined, with a relative error not exceeding $\pm 1\%$.

3. Tin was determined polarographically in a supporting electrolyte 3*N* in sodium chloride and 1*N* in hydrochloric acid, with 0·001% Triton X-100 present as maximum suppressor. The composition of the supporting electrolyte was dictated by the eluent employed for tin (6*N* sodium hydroxide solution). Seven mg of tin per litre could still be determined with a relative error not exceeding $\pm 1\%$.

4. Copper was determined spectrophotometrically, employing ferrocyanide.[15]

Based on the above, the following procedure is suggested for the separation of lead, copper, antimony and tin:

0·1 ml of the sample, containing up to 400 μg of each metal and 7*N* in hydrochloric acid, is introduced on top of the resin column, followed by two successive portions of 0·2 ml each of 7*N* hydrochloric acid. The following eluents are now passed through the column at the rate of 3 ml per min: 5·2 ml of 7*N* hydrochloric acid (lead fraction), 5·2 ml of 1·56*N* hydrochloric acid (copper fraction), 7·7 ml of 1*N* hydrofluoric acid, 0·3*N* in hydrochloric acid (antimony fraction), 1 ml of 7*N* hydrochloric acid (to be discarded; this serves to remove hydrofluoric acid from the column), and 10 ml of 6*N* sodium hydroxide solution (tin fraction).

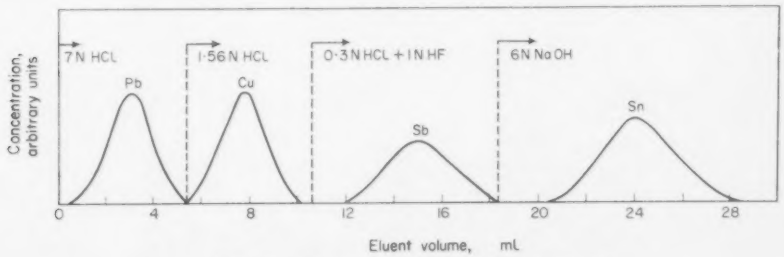

FIG. 10.—The separation of the four elements.

The eluents are passed through the column in the order given, each fraction being collected separately and analysed by the methods specified above.

For the analysis of alloys, 0·1–0·3 g of the alloy are dissolved in 15 ml of concentrated hydrochloric acid, with the dropwise addition of 3 ml of 30% hydrogen peroxide and heating. After complete dissolution, excess hydrogen peroxide is removed by boiling, the solution is cooled and 0·3 g of sodium sulphite are added. Two short glass capillaries are introduced, the solution is boiled to remove sulphur dioxide and is made up to 25 ml with concentrated hydrochloric acid. An aliquot of this solution is now introduced on top of the resin column and eluted according to the procedure suggested above.

Zusammenfassung—Die selektive Sorption der negativ geladenen Komplexionen von Zinn, Antimon, Blei und Kupfer an einem Anionenaustauscher wurde herangezogen um die Metalle voneinander quantitativ zu trennen. Die Methode wurde zur Analyse von Legierungen verwendet.

Résumé—La fixation sélective des complexes anioniques de l'étain, de l'antimoine, du plomb et du cuivre sur une résine échangeuse d'anions a été utilisée pour leur séparation quantitative. La méthode a été ensuite adaptée à l'analyse des alliages.

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THE SELECTIVE DETERMINATION OF ACTIVE HYDROGEN WITH DISPERSED SODIUM

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Summary—Sodium in the dispersed state has been found to be a selective reagent for the determination of active hydrogen in acids, alcohols, phenols, amides and sulphonamides. The pressure change in a constant-volume system caused by the evolution of gaseous hydrogen is measured after a sample is treated with an excess of dispersed sodium. Under the same conditions, amines, aldehydes, ketones, esters and 1-acetylenes do not produce any hydrogen.

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THE many methods available[1,2,4,7,9–11] for the determination of active hydrogen in organic compounds share the characteristic that each technique determines the total active hydrogen present without regard to the particular type of compound represented. Such a lack of selectivity is a distinct drawback to active hydrogen analysis.

In the procedure developed here, three methods of determination are used to separate the compounds containing active hydrogen into three classes of reactivity. The first two methods use a dispersion of metallic sodium in an inert medium as the reagent, while the third method can be any of the conventional, undifferentiating procedures.

The most reactive group of compounds containing active hydrogen is that comprising the acids, alcohols and some phenols, which can be determined by adding an excess of a standardised dispersion of sodium to a weighed sample dissolved in xylene, and converting the excess sodium to sodium ethoxide with an excess of ethyl alcohol. The sodium ethoxide is titrated with a standard acetic acid solution, and the amount of sodium consumed by the organic acid or active phenol is found by difference. The details of this procedure have been published.[6]

The sum of the active hydrogen due to the most reactive group of compounds and the group of intermediate reactivity, including acetylated amines, sulphonamides and the remainder of the phenols, can be determined by the procedure described in detail in the experimental part of this paper.

The sum of all types of active hydrogen can be determined by any of the conventional procedures, such as the Zerewitinoff method or the lithium aluminium hydride method. By difference one can ascertain the amount of active hydrogen contained in the least reactive group, which includes aldehydes, ketones, amines, esters and 1-acetylenes.

In the procedure described here for the determination of the sum of the highest and intermediate reactivity groups, an excess of dispersed sodium is allowed to react with either a pure liquid sample or a solution of a solid sample in an inert solvent, and the evolved hydrogen is determined by measuring the pressure change when the reaction is carried out in a constant-volume system.

EXPERIMENTAL

Reagents

Commercially available reagent-grade chemicals were used when possible. Solvents were purified by refluxing over sodium, followed by distillation. Samples were the best grade available and were used without further treatment in most cases.

Dispersed sodium: The dispersions of sodium were prepared using the apparatus described by U.S. Industrial Chemicals Co.,[8] modified by passing the stirrer shaft through a ball bearing instead of through the Oilite bushing, and omitting the thermometer. Periodic replacement of the ball bearing was necessary, as the condensing solvent vapours gradually removed the grease. Two hundred and fifty ml of xylene, 10 drops of oleic acid and approximately 2 g of sodium were added to a 500-ml three-necked creased flask, which was then mounted in the apparatus and allowed to heat. When the sodium had melted, the mixture was stirred at about 12,000 rpm for 10 min. The resulting dispersion was allowed to cool, with care being taken not to agitate the mixture during cooling, in order to prevent coagulation. Dry, oxygen-free nitrogen was passed over the contents of the flask throughout these operations.

When cool, the dispersions were diluted with 500 ml of either xylene or dioxan, and a second 10 drops of oleic acid were added. The diluted dispersion was refluxed overnight while protected from moisture with a Drierite drying tube.

A freshly shaken dispersion may be satisfactorily pipetted with only the normal precautions for a corrosive liquid.

Apparatus

Measurements of pressure change caused by liberated hydrogen were carried out in a cylindrical glass vessel 40 cm long and 4 cm in diameter, topped by a 34/28 standard taper joint with a long tube sealed in it. The inner tube extends to within a few cm of the bottom, to accomodate a 1-ml ampoule which is supported by a brass plate held to the bottom of the inner tube by means of four springs attached to hooks on the outer side of the tube. The tube extends 25 cm above the joint to accomodate a pointed iron striker which is held in place by an external magnet. A side arm near the top of the vessel leads to a vacuum line, an outlet to the air, and a mercury manometer. The vessel is mounted in a constant-temperature bath. A magnetic stirrer placed below the water bath permitted the sodium to be kept in suspension.

Procedure

The measurements were carried out by sealing a weighed sample in an ampoule, mounting it in the apparatus containing 100 ml of dispersed sodium, applying vacuum to the system until solvent ebullition commenced, and closing the system. In 20 min to 1 hr a constant pressure reading may be obtained on the manometer, at which time the striker is allowed to fall, breaking the ampoule and initiating the reaction. When constant pressure is again attained, the result is noted.

Calibration

Seven samples of Baker and Adamson reagent-grade methanol and six samples of Matheson, Coleman and Bell Spectroquality methanol were measured by the foregoing procedure and assumed to contain 1·00 active hydrogen. From the weights of the samples and their corresponding pressure changes the volume of the system was calculated. Blanks were determined and found to produce 4 mm pressure change.

Calculation

The weight of the sample and the corresponding pressure change, corrected for the blank, along with the temperature, molecular weight and volume of the system, were used to calculate the number of active hydrogens present per molecule.

Choice of conditions

Experiments under a variety of conditions showed that solid samples did not react satisfactorily, probably because the inner parts of the solid did not come into contact with the sodium. Liquid samples were found to react satisfactorily, and solids were determined successfully if dissolved in

dioxan. The dispersion was found to be most suitable when prepared in a mixture of 2 parts of dioxan to 1 part of xylene by volume. Apparently the solvent power of dioxan for the salt-like products formed was necessary to prevent these products from coating the sodium particles before reaction was complete. Dispersions in dioxan alone were not used, as it was felt that finely divided sodium floating to the top of the dispersion medium upon standing created a situation too hazardous for routine determinations.

RESULTS AND DISCUSSION

Table I shows the number of active hydrogens found for a variety of compounds and the average error for the determinations, calculated as the difference between the pressure change found and the pressure change expected for the sample if it contained an integral number of active hydrogens.

TABLE I. VALUES OF ACTIVE HYDROGEN DETERMINED

Compound	Number of Determinations	Average amount taken, *m moles*	Average active hydrogen	Average error of pressure change (absolute value)
Ethanol	1	4·306	0·98	2·2
t-Butyl alcohol	2	3·867	1·00	2·8
Acetic acid	3	6·029	0·999	2·2
n-Butyric acid	2	4·609	0·99	1·0
Benzoic acid	2	2·040	0·85	9·1
Salicyclic acid	2	2·087	1·04	2·4
Resorcinol	8	1·413	1·62	13·0
Aniline	1	3·599	0·09	9·2
n-Butylamine	6	3·368	0·06	5·6
2,4-Dimethylphenol	2	2·688	1·10	7·6
o-Nitrophenol	7	0·979	0·68	9·1
4-Chloro-3-methylphenol	2	1·711	0·89	9·0
2,4-Dinitrophenol	2	0·960	0·92	2·2
Cyclohexanone	4	2·973	0·18	15·9
1-Hexyne	1	3·488	0·003	0·3
n-Butyraldehyde	1	5·327	0·03	4·2
Ethyl acetate	2	3·698	0·04	4·9
Acetone	2	4·640	0·03	3·2
Benzonitrile	1	3·021	0·000	0·6
Azobenzene	1	0·368	0·000	2·2
Bromobenzene	1	3·351	0·000	0·1
Acetanilide	2	0·796	0·87	3·0
Sulphanilamide	3	0·693	0·91	4·9

As a measure of the precision of the method of obtaining the pressure change, the methanol values used to calibrate the volume of the system were re-calculated on the basis of the average volume, and the error in pressure change was found for each sample. The sum of the squares of these errors divided by one less than the number of measurements was used to establish a 95% confidence limit for the error in the pressure change by use of a one-tailed chi square test. Errors in the pressure change greater than the limit found, 11·3 mm, represent errors that could not be accounted for by the pressure measuring device, a metre-stick manometer. Comparison of this value with the average error recorded for each substance in the Table shows that all of the measurements are well within the experimental error of an integral value with the

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exception of resorcinol and cyclohexanone. Similar results for these two compounds have been previously reported.[3,5] The relatively large deviation from theoretical integers with a small experimental error reported for *o*-nitrophenol and acetanilide are due to the limited solubility of the compounds. These small sample sizes caused pressure changes of about 25 mm of mercury, while larger samples of liquids or more soluble solids caused pressure changes as great as 200 mm. Since the errors in measurement were essentially constant, the relative error in the small samples, which is seen as the deviation of the number of active hydrogens from an integer, is considerably greater than for compounds for which larger samples could be used.

The essentially constant errors suggest that the largest errors are independent of the particular substance being determined. A consideration of the various sources of experimental error indicates that the primary cause of poor precision is in the reading of values on the manometer. The manometer used for this exploratory work was a 4 mm glass capillary bent in the form of a U around a metre-stick and filled with mercury. It is to be anticipated that the use of a more precise manometer with the present system will yield values having a precision of 1 to 2% for small samples and a few parts per thousand for liquids and readily soluble solids. In fact the use of a differential dibutylphthalate manometer might enable even the more difficultly soluble materials to be run with a precision of about 0·5%.

It is particularly of interest to note that aniline and n-butylamine do not give any appreciable reaction in this method, thus permitting the differentiation of less reactive types of active hydrogen compounds from the more reactive ones. Extensive studies were made to determine conditions under which amines would react. At the boiling point of xylene, amines were found to be still unreactive. The presence of ferric oxide or chloride, aluminium oxide or chloride, or zinc chloride did not cause amines to show reaction. Sodium dispersions in xylene, tri-n-butylamine, and xylene-dioxan mixtures were equally ineffective in causing amines to react.

Since a back-titration procedure using dispersed sodium can be applied to acids, alcohols and some phenols,[6] it is possible to classify active hydrogen compounds into three reactivity types. The first class are those which can be determined by the back-titration procedure. The second class, some phenols, acetylated amines and sulphonamides are those which show reaction by the procedure presented here but not by the back-titration procedure. Finally, the class of amines, aldehydes, ketones, esters and 1-acetylenes are those which do not react with dispersed sodium but can be determined by a Zerewitinoff method.

Zusammenfassung—Natrium in fein dispergierter Form hat sich als selektives Reagens zur Bestimmung des aktiven Wasserstoffes in Amiden, Alkoholen, Phenolen und Sulfonamiden erwiesen. Die Druckänderungen in einem volumkonstanten System werden gemessen, nachdem die Probe mit dispergiertem Natrium reagiert hat. Unter diesen Bedingungen produzieren Amine, Ketone, Aldehyde, Ester und 1-Acetylene keinen Wasserstoff.

Résumé—Les auteurs ont montré que le sodium, à l'état dispersé, était un réactif sélectif pour le dosage de l'hydrogène actif dans les acides, les alcools, les phénols, les amides et les sulfonamides. La variation de pression, dans un système à volume constant, provoquée par le dégagement de l'hydrogène gazeux, est mesurée après qu'un échantillon ait été traité par un excès de sodium dispersé. Dans les mêmes conditions, les amines, les aldéhydes, les cétones, les esters et les 1-acétylènes ne produisent pas d'hydrogène.

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ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—I

PRINCIPLE AND THEORY OF THE METHOD

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Summary—The proposed method serves for the selective determination of trace amounts of metals. The analytical procedure consists of a single extraction of the metal to be determined, in the form of a complex with an organic reagent, and measuring the radioactivity of the extract obtained. The amount of the organic reagent employed must always be less than would correspond to the stoichiometric ratio. A theoretical evaluation of the extraction is given for these conditions, from which the conclusion may be drawn that a number of metals may thus be determined with greater selectivity than in a conventional extraction with a stoichiometric excess of organic reagent. On the basis of the relation obtained, conditions have been predicted for the determination of many elements. The possibilities of the selective determination of metals in the presence of interfering metals are also discussed.

INTRODUCTION

ISOTOPIC dilution analysis is based on the determination of the change of specific activity caused by mixing a radioactive and a non-radioactive isotope of the element analysed. This method, the foundations of which were laid down by Hevesy and Hobbie[1] and by Starik[2] more than 25 years ago, has previously been used more often in organic analysis and in biochemistry than in the analysis of inorganic systems, where it has been used relatively seldom. Its greatest advantage over all other analytical methods is, that in order to carry out the analysis only a part of the component to be analysed need be isolated in a pure state, and only the change of the isotopic composition of this part need be determined.

The method of isotopic dilution would be of great importance for trace analysis not only for its high sensitivity, but also because the quantitative separation of the analysed component, present in such small amounts, is otherwise very difficult. The use of the dilution method has up to now been rendered difficult in these cases by the procedure employed, which necessitated the determination of specific activity. Thus, it was necessary to isolate an amount of the substance sufficient to make it possible to determine not only its radioactivity but also its amount. The sensitivity of the analysis was therefore limited by the sensitivity of the method by which the isolated amount was determined. In most of the published methods, precipitation or electrolysis were used for isolation and the isolated amount was either weighed or determined by some other analytical procedure. The amount of the element to be determined was then calculated by the relation:[1,2]

$$x = y\left(\frac{A_1}{A_2} - 1\right) \qquad (1)$$

where y is the amount of radio-isotope used, A_1 is the specific activity of the radio-isotope, and A_2 is the specific activity of the mixture of radio-isotope and added analysed element. Specific activity is equal to the ratio of absolute activity and amount of sample measured, *i.e.*

$$A_1 = \frac{a_1}{m_1} \quad \text{and} \quad A_2 = \frac{a_2}{m_2}$$

where a_1 and a_2 are the absolute activities, and m_1 and m_2 are the isolated amounts.

If we always isolate the same amounts of the substance from the solution of original activity and from the solution obtained by dilution with the non-active determined element (*i.e.* $m_1 = m_2$), then in relation (1) the specific activities may be replaced directly by relative activities, measured under the same conditions. Therefore it is not necessary to know the values m_1 and m_2, since for calculation of the amount of the element to be determined it is sufficient to know the relative activities and the amount of radio-isotope added to the analysed solution.

Development of isotopic dilution analysis into the region of trace amounts therefore depends on the development of methods by which equal and very small amounts may always be isolated with high precision and reproducibility. In general this may be done by extraction, chromatography, electrolysis, precipitation or adsorption on surfaces of equal areas. From the results of work published up to now[3–7] and from the results described a further paper,[8] the most suitable methods are seen to be extraction and electrolysis. The use of ion-exchangers for this purpose will probably also be very advantageous.

THEORY

In order always to extract the same amount of the complex of the metal and the organic reagent from solutions containing various concentrations of this metal, it is necessary always to use a smaller amount of the organic reagent than corresponds to the stoichiometric ratio. The conditions of the extraction in this case may in general be determined from the fundamental equation of the extraction process:

$$M^{N+} + N(HA)_{org} \rightleftarrows (MA_N)_{org} + NH^+. \tag{2}$$

The equilibrium constant of this process, K, is given by:

$$K = \frac{[MA_N]_{org}[H^+]^N}{[M^{N+}][HA]^N_{org}} \tag{3}$$

where the subscript *org* denotes the organic phase. By inserting the equilibrium concentrations of the complex MA_N and of the reagent HA in the organic phase, the concentration of the metal M in the aqueous phase and the value for K in relation (3), the value of the threshold pH may be calculated, at which always the same amount of metal can be extracted.

The equilibrium concentration of the complex MA_N is determined from the condition that more than 99·9% of the organic reagent HA has been used up in forming the complex MA_N, *i.e.*

$$[MA_N]_{org} \cdot V_{org} \geqslant 0{,}999 \frac{c_{HA}}{N} \cdot V_{org} \tag{4}$$

where V_{org} is the volume of the organic phase, and c_{HA} is the original concentration of

the reagent in the organic phase. This condition guarantees the isolation always of the same amount of metal with a precision of better than 0·1 %.

The equilibrium concentration of the metal M is determined from the relation:

$$[M] \cdot V = c_M \cdot V - \frac{c_{HA}}{N} \cdot V_{org} \tag{5}$$

where V is the volume of the aqueous phase, and c_M is the original concentration of the metal in the aqueous phase.

For the equilibrium concentration of the organic reagent it is found that:

$$[HA]_{org} \cdot V_{org} \leq 0{,}001\ c_{HA} \cdot V_{org}. \tag{6}$$

By solving equations (3), (4), (5) and (6) the value of the threshold pH is:

$$pH \geqslant \frac{1}{N} \cdot \log \frac{c_{HA}}{N} - \frac{1}{N} \log \left[c_M - \frac{c_{HA} V_{org}}{NV} \right] - \frac{1}{N} \log K - \log 0{,}001 c_{HA} \tag{7}$$

Expression (7) is precisely valid only in the case where the dissociation of the organic reagent in the aqueous phase may be neglected, *i.e.* when $V \cdot [A^-] < [HA]_{org} \cdot V_{org}$. This condition is fulfilled for a hydrogen ion concentration

$$[H^+] > K_{HA} \cdot q_{HA}^{-1} \frac{V}{V_{org}} \tag{8}$$

where K_{HA} is the dissociation constant of the organic reagent, and q_{HA} is the distribution coefficient of the organic reagent.

For the extraction of metals by a solution of dithizone in carbon tetrachloride, the threshold hydrogen ion concentration, calculated according to equation (7), must be higher[9,10] than $10^{-9} \frac{V}{V_{org}} \left(K_{HA} \cdot q_{HA}^{-1} = 10^{-9} \right)$. When the threshold hydrogen ion concentration is less than $10^{-9} \frac{V}{V_{org}}$, dithizone dissociates in the aqueous phase to such an extent that the condition expressed by relation (4) cannot be fulfilled.

From an analysis of relation (7) it is evident that the first two terms on the right-hand side have relatively little influence on the value of the threshold pH. If, for example, the amount of organic reagent is less than half that which would correspond to the stoichiometric ratio, the sum of these two terms for $V_{org} = V$ is zero; if the amount of organic reagent is ten times lower, it is equal to $-1/N$ *etc.* A far greater influence on the value of threshold pH is exerted by the last two terms of equation (7). For the determination of microgram amounts of metals, concentrations of the organic reagent of 10^{-4} and less are used, the value of $-\log 0{,}001\ c_{HA}$ is therefore $\geqslant 7$. In order to obtain a threshold pH value which is not too high, one can use for the determination of metal traces by the proposed method only complexes whose value of $-(1/N) \cdot \log K$ is sufficiently low. This condition is best fulfilled by some dithizonates, cupferrates *etc.*[9] The limitation mentioned, on the other hand, results in an increased selectivity for the various determinations.

In Table I the K values for dithizonates of various metals, threshold pH values and suitable isotopes are listed for the determination of various elements by this method. Threshold pH values have been calculated according to relation (7) for a double

excess of metal, for $c_{HA} = 10^{-4}M$ and $V/V_{org} = 10$. The pH region for the determination of a certain metal is limited on the alkaline side partly by the formation of insoluble hydroxides and in the case of dithizonates also by the formation of insoluble secondary dithizonates.[10] Hydrolysis of metals may be eliminated by the use of

TABLE I.—THE *K*-VALUE OF METAL DITHIZONATES AND THE PREDICTED pH VALUES OF DETERMINATION

Element	*K* (Reference)	$-\frac{1}{N}\log K$	pH of determination	Suitable isotope (half-life)[12]
Pd^{2+}			to 4*	
Hg^{2+}	$5{\cdot}7 \times 10^{26}$ (13) $7{\cdot}1 \times 10^{26}$ (14)	−13·4	−6 to 4*	^{203}Hg (46·5 d)
Pt^{2+}			to 4*	
Ag^{+}	4×10^{7} (15) 9×10^{8} (13)	−7·6 −8·9	0 to 7*	^{110}Ag (270 d)
Po^{2+}				
Cu^{2+}	$3{\cdot}6 \times 10^{9}$ (13) 3×10^{10} (16)	−4·8 −5·2	2·5 to 5*	
Bi^{3+}	$3{\cdot}5 \times 10^{9}$ (13)	−3·6	>4·0	RaD + RaE (25 y)
Au^{3+}			to 4*	
In^{3+}	$6{\cdot}9 \times 10^{4}$ (17)	−1·6	>6·0	^{114}In (50 d)
Zn^{2+}	5×10^{2} (18)	−1·3	>6·2	^{65}Zn (250 d)
Cd^{2+}	$1{\cdot}4 \times 10^{2}$ (18)	−1·1	>6·4	^{115}Cd (43 d)
Pb^{2+}	17 (18)	−0·6	>6·9	RaD + RaE (25 y)
Ni^{2+}	$2{\cdot}4 \times 10^{-1}$ (13)	+0·3	>7·8	
Sn^{2+}	9×10^{-3} (13)	+1·0	>8	^{123}Sn (125 d)
Fe^{2+}			—	
Tl^{+}	$4{\cdot}6 \times 10^{-4}$ (17)	+3·3	—	
Mn^{2+}			—	

* At higher pH a secondary very slightly soluble dithizonate is formed.[10]

complexing agents such as tartrates, cyanides, *etc.* Under these conditions the metal is present in the aqueous phase as a non-extractable complex MB_s, which is in equilibrium with free cations of the metal. The extraction constant of the process is in this case equal[11] to:

$$K' = \frac{[MA_N]_{org}[H^+]^N}{([M^{N+}] + [MB_s])[HA]^N_{org}} = \frac{[MA_N]_{org}[H^+]^N}{[M^{N+}](1 + K_s'[B^-]^s)[HA]^N_{org}} = \frac{K}{1 + K_s'[B^-]^s} \quad (8)$$

where

$$K_s' = \frac{[MB_s]}{[M^{N+}][B^-]^s}$$

and $[B^-]$ is the equilibrium concentration of the anion of the complexing agent.

By inserting relation (8) into relation (7) we obtain:

$$pH \geqslant \frac{1}{N}\log\frac{c_{HA}}{N} - \frac{1}{N}\log\left[c_M - \frac{c_{HA}}{N}\frac{V_{org}}{V}\right] - \frac{1}{N}\log K + \frac{1}{N}\log(1 + K_s'[B^-]^s) - \log 0{\cdot}001c_{HA}. \quad (9)$$

The threshold pH value is increased in the presence of a complexing agent, but on the other hand determinations may be carried out at even high pH values.

DISCUSSION

Selectivity of the method

Each organic reagent forms extractable complexes only with a certain number of metals. It is therefore evident that an extractable metal can be determined in the presence of any excess of non-extractable metals. For instance, each of the elements listed in Table I can be determined in the presence of all metals not named in this table, that is in the presence of all metals which are not extracted by dithizone.

A selective determination of a certain metal may be worked out, however, even in the presence of metals which also form extractable complexes with the reagent employed. The concentration ratio of two metals in the organic phase is easily determined from the individual K values. For instance, from the values of K for mercury and copper dithizonates (Table I):

$$\frac{[HgA_2]_{org}}{[CuA_2]_{org}} = \frac{10^{26}[Hg^{2+}]}{10^{10}[Cu^{2+}]}.$$

In this case the ratio $[HgA_2]_{org}/[CuA_2]_{org}$ is independent of pH and $[HA]_{org}$. The concentration of mercury in the organic phase will therefore be 10^{16} times higher than the concentration of copper, but in the presence of excess dithizone both of these elements are extracted together.[10]

For silver and copper dithizonates (Table I):

$$\frac{[AgA]_{org}}{[CuA_2]_{org}} = \frac{10^{8}[Ag^{+}][H^{+}]}{[Cu^{2+}][HA]_{org}10^{10}}.$$

In this case the charges of the elements which are to be separated are different, and the ratio $[AgA]_{org}/[CuA_2]_{org}$ depends on pH as well as on $[HA]_{org}$. In carrying out the extraction at pH = 0 by a dithizone solution of concentratiou $10^{-4}M$ ($[HA]_{org} \leq 10^{-7}M$, see relation (6)), the following holds:

$$\frac{[AgA]_{org}}{[CuA_2]_{org}} \geqslant 10^{5}\frac{[Ag^{+}]}{[Cu^{2+}]}.$$

It should therefore be possible to extract silver with sufficient precision even in the presence of a one hundred-fold excess of copper, but on the other hand at pH = 0, in the presence of excess dithizone, both elements are extracted together.[10]

From the above it is evident that the metal complex having the highest value of K can be selectively separated from the other metals which form extractable complexes with the given organic reagent. Thus, for instance, the selective separation of mercury in the form of a dithizone complex may be expected (only palladium interferes, see Table I); of iron^{III} in the form of a complex with thenoyltrifluoroacetone or acetylacetone; of gallium^{III} in the form of a complex with 8-hydroxyquinoline, *etc.*

If the K values of separated complexes are near to each other or if the K value of the interfering complex is higher than that of the determined complex, a selective separation may even then be obtained by the addition of a further complexing agent, which forms a non-extractable complex with the interfering ion.

From the values of K we see, for instance, that in the determination of bismuth by dithizone palladium, mercury, silver and copper interfere (see Table I). In the presence of cyanide ions, however, these ions do not interfere, because stable cyanide

complexes are formed. Thus, in the determination of bismuth in the presence of mercury at pH = 9 and $[CN^-] = 10^{-2}$ *M* from relation (3):

$$\frac{[BiA_3]_{org}}{[HgA_2]_{org}} = \frac{10^9[Bi^{3+}][HA]_{org}^3\, 10^{34}}{10^{26} \cdot C_{Hg}\,[H^+]}$$

where $C_{Hg} = [Hg^{2+}] + [Hg(CN_4^{2-})] = [Hg^{2+}](1 + K'_{Hg(CN)_4^{2-}} \cdot [CN^-]^4)$

$(K'_{Hg(CN)_4^{2-}} = 10^{42})$.[19]

In the presence of cyanide ions there will be a far larger amount of bismuth in the organic phase, even in the presence of excess mercury^{II} ions. As we see from the values of *K* for lead and tin dithizonates, these elements will not interfere in the determination of bismuth by this method, though in the conventional extraction procedure in cyanide medium these two elements interfere,[10] for like bismuth they form only very weak cyanide complexes.

Similarly, the influence of interfering metals may be eliminated by the use of precipitating agents. For example, diethyldithiocarbamate forms sparingly soluble crystalline precipitates with most metals, except zinc. If the solubility products of these precipitates are known, the influence of interfering metals can easily be determined. Thus, for the extraction of zinc in the presence of mercury and diethyldithiocarbamate:

$$\frac{[ZnA_2]_{org}}{[HgA_2]_{org}} = \frac{[Zn^{2+}]10^2}{[Hg^{2+}]10^{26}} = \frac{P_{Zn} \cdot 10^2}{P_{Hg} \cdot 10^{26}}$$

where P_{Zn} and P_{Hg} are the solubility products.

Because $P_{Hg} \ll 10^{-26}\, P_{Zn}$, it is possible to determine zinc even in the presence of mercury.[20,21]

Limitations of the method

The use of the proposed method for the determination of amounts of metals larger than 1 mg is not advantageous, because physicochemical analytical methods may be used whose precision is, under these conditions, better than the precision of radiometric methods, which is controlled by the statistical character of radioactive decay. The sensitivity of the method is limited by two factors: (a) the organic reagent employed cannot be diluted infinitely, and (b) at present there are not radio-isotopes of sufficiently high specific activity at hand for all cases. The latter limitation will doubtless be solved by the development of a procedure for the preparation of carrier-free radio-isotopes.

CONCLUSION

On the basis of the principle described, a number of selective determinations of trace amounts of metals in the form of complexes with various organic reagents can be worked out. Up to now the proposed method has been used for the selective determination of zinc in amounts of the order of 10^{-6} to 10^{-9} g/ml.[8]

As was said at the beginning of this paper, a separation of similar amounts may also be carried out using ion-exchangers. The principle of this method is as follows: to the solution, which contains a number of metals, add a complexing agent which forms with the metal to be determined the most stable neutral or negatively charged complex. If the amount of added complexing agent (for instance EDTA) is lower than

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that which corresponds to the stoichiometric ratio, then by passing this solution through a cation-exchange column the same amount of metal complex can always be isolated, which fact may be used for the determination of metal traces by isotopic dilution analysis.

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Zusammenfassung—Extraktionsmethoden im Verein mit Isotopenverdünnung erlauben die selektive Bestimmung von Metallspuren. Die Analyse besteht aus einer einzigen Extraktion des Metalles als Komplex mit einem organischen Komplexbildner in eine organische Phase und anschliessende Zählung der Radioaktivität der isolierten organischen Phase. Die Menge an organischem Komplexbildner muss immer kleiner sein, als stöichiometrisch nötig. Eine theoretische Behandlung und Erklärung dafür wird mitgeteilt. Es wird gezeigt, dass die Selektivität unter solchen Bedingungen höher ist, als wenn nach der üblichen Art mit Reagensüberschuss gearbeitet wird. Auf grund der Ableitungen wurden die optimalen Bedingungen für verschiedene Systeme vorausgesagt. Die Möglichkeiten in Anwesenheit von Störmetallen zu arbeiten werden ebenfalls diskutiert.

Résumé—L'analyse par dilution isotopique associée à l'extraction par solvant peut servir au dosage sélectif de traces de métaux. La méthode analytique consiste en une simple extraction du métal à doser sous forme d'un complexe avec un réactif organique, et d'une mesure de la radioactivité du produit obtenu. La quantité de réactif organique employé doit toujours être inférieure à celle correspondant au rapport stoechiométrique. Une évaluation théorique de l'extraction est donnée pour ces conditions; on peut conclure qu'un certain nombre de métaux peut être ainsi dosé avec une plus grande sélectivité que dans l'extraction conventionnelle par un excès stoechiométrique de réactif organique. En se basant sur la relation obtenue, les auteurs ont prévu les conditions de dosage d'un certain nombre d'éléments. Les possibilités de dosage en présence de métaux gênants sont aussi discutées.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH NITRILOTRIACETIC ACID

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Summary—Palladium^{II} in aqueous solution yields with nitrilotriacetic acid a complex which is suitable for the spectrophotometric determination of this element. The other platinum metals interfere when present in appreciable amounts. The influence of pH, ionic strength, and palladium and nitrilotriacetic acid concentrations are investigated. Evidence is given for the presence of a bico-ordinated palladium complex.

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UNLIKE that of other metals, the behaviour of the noble metals with complexones is only slightly known. This is due to the fact that the platinum group metals either cannot form complexes with ligands of this type or can only do so in special conditions. Palladium, the least noble among the metal ions of the platinum group, is able to form complexes with ethylenediaminetetra-acetic acid (EDTA) as Hynes *et al.*,[1] Flaschka[2] and MacNevin and Kriege[3] have pointed out. The last two authors, in a later work[4] affirm that iridium^{IV} can also be complexed by EDTA in strongly alkaline media.

In a wide investigation, which is being carried out in this Institute[5,6] for analytical purposes, of the behaviour of the noble metals with several ligands, a study of palladium complexes with nitrilotriacetic acid (NTA) has seemed worth while. The lack of publications on the behaviour of NTA with noble metals has to be taken into account, as well as the ability of this ligand, in some cases,[7] to form complexes with a metal-ligand ratio other than 1:1.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman DU spectrophotometer, 1-cm silica cells being used.

Reagents

Palladium solution: Prepared by dissolving $PdCl_2$ in 0·1*M* hydrochloric acid and diluting, to give 530 μg of Pd^{2+}/ml. The solution was standardised gravimetrically with dimethylglyoxime.

Nitrilotriacetic acid: This solution, after neutralisation with sodium hydroxide, was standardised with magnesium^{II} solution.

Solutions of other noble metals were prepared by diluting standard solutions prepared from $IrCl_4$, $IrCl_3$, H_2PtCl_6, $RuCl_3$, and Na_3RhCl_6.

RESULTS

In a hydrochloric acid medium a deep red-brown chloro complex is formed when palladium^{II} is present, becoming yellow in colour in very dilute solutions. In the violet and ultraviolet range a sharp absorption appears. On adding a small amount of NTA to these solutions, a non-visible reaction occurs, although a noticeable variation in the spectrum can be observed, as is shown in Fig. 1: the maximum is shifted towards a shorter wavelength and the absorption increases greatly; on the whole, the

spectrum appears to be altered appreciably. It is evident that palladium^{II} has been complexed by NTA. When the ligand concentration increases, the colour of the solution decreases slightly.

The palladium^{II}–NTA complexes can be formed either in acidic, neutral or alkaline media, as shown in Fig. 2. A considerable change of the absorption maximum is observed when the hydrogen ion concentration is altered. In the range pH 0–3 the absorbance increases remarkably with pH. On the other hand, in the range pH 3–11 the absorbance is constant, and it decreases above pH 11. As is shown in Fig. 3, a spectrophotometric determination can be performed by adjusting the solution to pH 3–11. The formation of the palladium-NTA complex is practically instantaneous: measurements carried out at several intervals on the same solutions have not shown any appreciable differences.

When plotting the optical density corresponding to the absorption maximum versus NTA concentration in a palladium^{II} solution at pH 7, an unusual curve is obtained. In fact, a maximum is reached (at 360 mμ) with a ratio of Pd: NTA = 1:1; with higher amounts of NTA a decrease is observed up to a ratio of 1:2. At the same time the absorption maximum is slightly shifted to a shorter wavelength. Beyond the latter ratio no noticeable variation is observed at 330 mμ, which is the wavelength of the new maximum.

A reliable interpretation of this phenomenon, which is illustrated in Fig. 4, appears to be as follows: in the presence of a low concentration of complexing agent, the 1:1 complex is firstly formed; with increasing NTA, a more co-ordinated complex is present in solution which presumably has a co-ordination number of 2. The ability of the palladium^{II} ion to co-ordinate two NTA molecules is not completely unexpected: the formation of the bico-ordinated complex depends on the relatively small volume of the ligand, particularly as compared with that of EDTA. Indeed, the only practical difference between these two complexing agents consists in the smaller dimensions of the former.

Adherence to Beer's law in the above mentioned range of pH is shown both by the monoco-ordinated and by the bico-ordinated complex. However, in the case of an analytical determination the ligand concentration must, of course, be higher than that necessary to give the 1:2 complex. A large excess of NTA does not interfere. A suitable analytical range is from 20 to 220 ppm of palladium. In Table I quantitative results are reported.

TABLE I.—DETERMINATION OF PALLADIUM WITH NITRILOTRIACETIC ACID

Pd taken, *ppm*	Pd found, *ppm*
20	20·2
28·5	28·1
53	52·3
79·5	80·1
106	107
132·5	134·1
159	157·8
185·5	184·5
212	213·2

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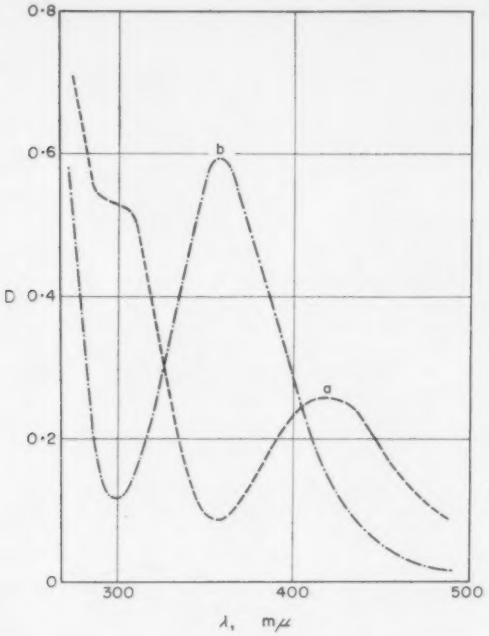

FIG. 1.—Absorbance curves for (a) palladium-chloro complex, and (b) palladium-NTA complex. (Pd = 106 ppm, pH = 7).

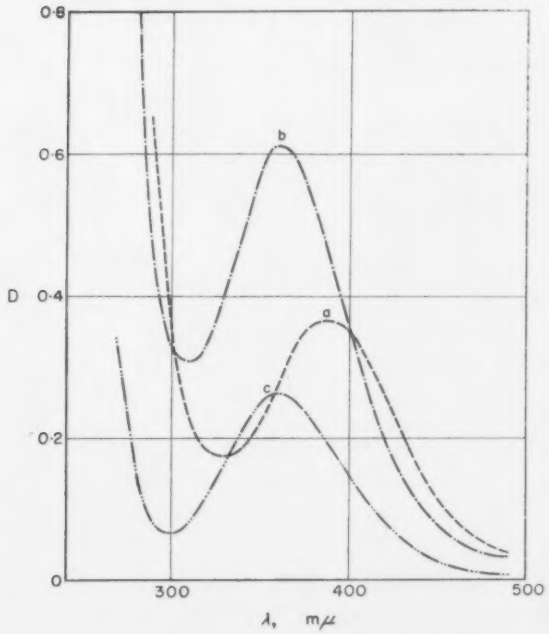

FIG. 2.—Absorbance curves for palladium-NTA complex at (a) pH 1·81, (b) pH 6·86, and (c) pH 11·93. (Pd = 106 ppm, Pd/NTA = 1:1).

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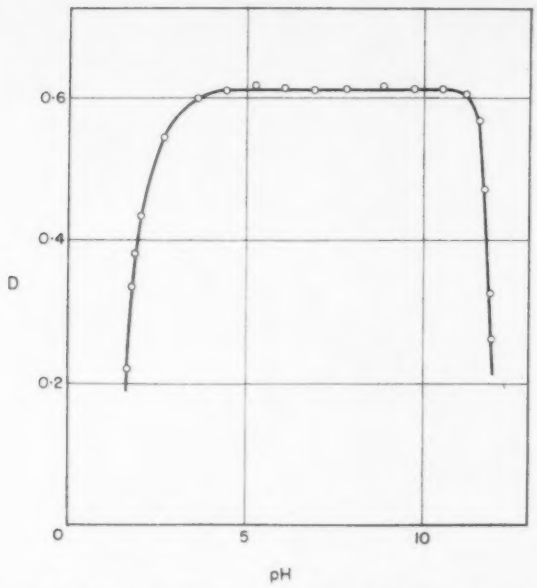

FIG. 3.—Absorbance maximum with change of pH for palladium-NTA complex (Pb = 106 ppm, Pd/NTA = 1:1).

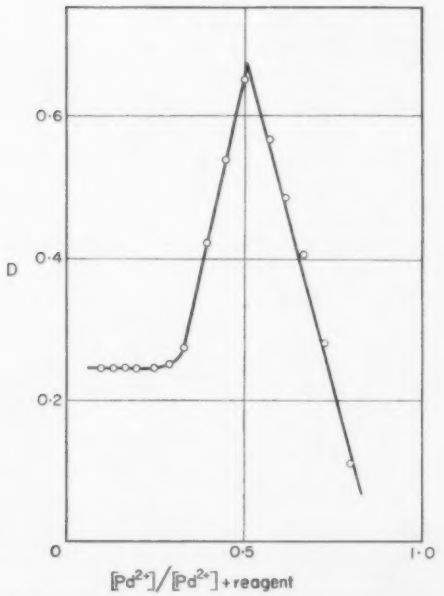

FIG. 4.—Job's method of evaluating the composition of the palladium-NTA complex.

The ionic strength has been maintained constant at about 0·1 by means of sodium perchlorate. An increase in the ionic strength does not involve any appreciable difference in the values of the maximum absorbance, as is shown by the results in Table II.

TABLE II.—EFFECT OF THE "IONIC STRENGTH" ON THE ABSORBANCE OF THE PALLADIUM-NTA COMPLEX (Pd = 106 ppm, Pd/NTA = 1:2).

Ionic strength	Optical density $\lambda = 330$ mμ
0·1	0·448
0·2	0·452
0·3	0·450
0·4	0·447
0·5	0·445

The use of a buffer, such as a phosphate one, to adjust the pH of the solutions in the range 5–9, is permissible. Measurements made after adjusting the solutions to the required pH range with sodium hydroxide, potassium hydroxide or with phosphate buffer yielded similar results.

Interfering ions

The metals of the platinum group interfere with the determination of palladium with NTA when they are present in appreciable amounts. The interferences were studied by observing the absorbance change taking place in a standard solution of

TABLE III.—TOLERANCE TO OTHER PLATINUM METALS

Ion	Limiting concentration, *ppm*
Ir^{IV}	19
Rh^{III}	89
Pt^{IV}	9·5
Os^{IV}	3·5
Ir^{III}	13
Pt^{II}	4·5
Ru^{III}	2

palladium^{II} containing an excess of NTA, on the addition of the other metals in the form of chloride solutions. The solutions were adjusted to pH 7 $\pm$ 0·5 with sodium hydroxide, potassium hydroxide or phosphate buffer. In Table III are reported the amounts of the other metals which produce a variation of 1% in the optical density. The interference of noble metals can be easily eliminated by separating the palladium^{II}

TABLE IV.—DETERMINATION OF PALLADIUM AFTER SEPARATION FROM Ir^{IV}, Pt^{IV} and Rh^{III} WITH DIMETHYLGLYOXIME

Taken, *mg*				Pd found, *mg*
Pd	Pt	Ir	Rh	
1	1	1	1	0·98
1	2	1	1	0·97
1	2	2	1	0·98
1	2	2	2	0·98

by precipitation with dimethylglyoxime according to the method of Ayres and Berg,[8] digesting the precipitate with *aqua regia*, and then evaporating the solution to dryness. The residue is taken up in dilute hydrochloric acid, and the solution is adjusted to pH 7 $\pm$ 0·5 after the addition of an excess of NTA. The absorbance is measured at 330 mμ. In Table IV are reported the results obtained by this method in the determination of palladium in the presence of appreciable amounts of platinum, iridium and rhodium.

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Zusammenfassung—Palladium(II) gibt mit Nitrilotriessigsäure in alkalischem Medium einen Komplex, der die photometrische Bestimmung des Metalles ermöglicht. Andere Platinmetalle stören, wenn in grösseren Mengen anwesend. Der Einfluss von pH, Konzentration der Reaktanten, sowie der Ionenstärke wurde studiert. Evindenz für einen bi-coordinierten Komplex wird erbracht.

Résumé—Le palladium (II) en solution aqueuse donne avec l'acide nitrilotriacétique un complexe qui peut être utilisé pour le dosage spectrophotométrique de cet élément. Les autres métaux de la mine du platine gênent quand ils sont en quantités appréciables. Les influences du pH, de la force ionique, des concentrations du palladium et de l'acide nitrilotriacétique ont été étudiées. Les auteurs montrent la présence d'un complexe bicoordonné du palladium.

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APPLICATIONS OF INFRARED SPECTROSCOPY—IV*

THE CAUSES OF ANOMALOUS ALKOXYL DETERMINATIONS GIVEN BY SUGARS AND POLYHYDRIC ALCOHOLS

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Summary—The volatile reaction products from Zeisel determinations on sugars and related compounds have been identified. One of the products from certain common sugars is 2,5 dimethylfuran, which interferes with the Vieböck iodometric determination of alkyl iodide, and has been shown to be a contributing cause of apparent alkoxyl values. Suggestions that hexyl iodide is evolved from sugars and that vinyl iodide is a product from polyhydric alcohols have been disproved.

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ZEISEL determinations on unmethylated sugars and polysaccharides have been reported[1,2] to give small apparent alkoxyl values. This implied that all carbohydrate materials would give slightly high analytical results, and made particularly difficult the interpretation of analyses of polysaccharide functions having a small but real methoxyl content.

In contrast, Goldstein and Smith[3] found that certain periodate oxidation products gave very high results. They proposed that the liberation of "extra" alkyl iodide from polyhydric alcohols such as glycerol was responsible. Von Rudloff[4] had earlier reported that polyhydric alcohols gave anomalous alkoxyl values. Strangely, he also obtained very unsatisfactory results for α-methyl-D-glucoside, a recommended reference standard[5] which gives excellent results.[6–9] Although it had been clearly established that the volatile products from ethylene glycol were ethylene + ethyl iodide, von Rudloff claimed that vinyl iodide + ethyl iodide were formed.

It is significant that the apparent methoxyl values quoted for standard compounds *e.g.* glucose and sucrose, ranged from zero to 0·4% (*cf.* refs. 1 and 2). Modification of Willstätter and Utzinger's trimethylamine technique[11] was found[1–3] to give results more satisfactory (although still high) than were obtained by the more convenient Vieböck iodometric titration. Recently, in a paper[13] which apparently repeats the published description[14] of a combustion method for alkoxyl determinations, Fukuda states that the method is not applicable to carbohydrates or related substances; the combustion method fails, in fact, for compounds liberating any non-acidic organic vapour in addition to alkyl iodides.

The identity of the volatile products from carbohydrate materials, and the sources of error contributing to the anomalous results, have hitherto not been clearly established. For simple sugars, Gran[2] showed that the apparent methoxyl content was not caused by traces of contaminating alcohols *etc.* He suggested that the formation of volatile hexyl iodides was responsible, although he could not identify or isolate such products.

* Part III—D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 1.

The proposals of von Rudloff and Gran were clearly based on inadequate experimental evidence: further investigation was desirable. Following our studies[9,15] of certain aspects of the Zeisel determination, it appeared that vapour-phase infrared spectroscopy could be applied to identify the volatile products from sugars and related compounds.

EXPERIMENTAL

Apparatus

The reagents, reaction conditions, and apparatus used for alkoxyl determinations were as described.[9] The technique for trapping volatile products, and details of the infrared method for their subsequent identification, have been given.[16,17]

Reagents

Glucose, sucrose, mannitol—all M.A.R.

5-Hydroxymethylfurfural was prepared by Haworth's method.[18]

5-Methylfurfural, furan, 2-methylfuran, 2,5-dimethylfuran and compounds not described in footnotes to Table I were commercial samples which conformed, after purification where necessary, to literature description.

Procedure

Samples (30–60 mg) of the compounds listed in Tables I and II were refluxed for 1 hr with hydriodic acid (6 ml, constant-boiling, pre-conditioned[9]) using nitrogen as flow-gas (6–8 ml per min.). The mixture of volatile products was collected, after passage through Anhydrone, in a trap immersed in liquid nitrogen. The components of each mixture were subsequently identified and quantitatively determined by vapour-phase spectroscopy[16,17]: since 2-iodohexane (b.p. 165°) was insufficiently volatile, it was identified as a pure liquid. All components were identified without difficulty; none of the mixtures was sufficiently complex for prior separation of the components by vapour-phase chromatography to be necessary.

RESULTS

Table I shows the products liberated in 1 hr from 30-mg to 60-mg samples of sugars and polysaccharide materials. The products from polyhydric alcohols are shown in Table II.

Effect of varying reaction-time and sample weights

The results obtained from experiments with glucose are shown in Table III.

Volatilisation of iodine

With 60 mg of glucose, only small amounts of iodine were released, insufficient to form a sublimate on the condenser walls: iodine did not pass the condenser. With 250-mg and 500-mg samples, however, extensive volatilisation occurred.[9] Although most of this condensed, some iodine reached the cold trap in which the volatile products were collected. The efficiency of removal of such quantities of iodine by 10% aq. sodium antimony tartrate in the B.S. design of scrubber[9] was therefore tested. When 100 mg of iodine were refluxed with pre-conditioned hydriodic acid, the amount of iodine passing the scrubber increased the reagent blank from 0·03 ml of 0·01*N* sodium thiosulphate to 0·06 ml (*cf.* ref. 8). When 500 mg of glucose was refluxed, the apparent methoxyl content found iodometrically was exactly equivalent to the amount of methyl iodide found by the infrared method in a duplicate run.

TABLE I

Compound*	Yield of volatile products†‡					
	n-Heptane	n-Hexane	n-Pentane	n-Butane	2,5 Dimethyl-furan	Acetone
Glucoheptose	tr	—	—	—	—	—
2-Deoxyglucose	—	tr	—	—	—	—
5-Hydroxymethylfurfural	—	tr	—	—	—	—
Glucose, hexoses	—	tr	—	—	2%	—
Fructose, sorbose	—	1%	—	—	2%	—
Rhamnose, fucose	—	1%	—	—	2%	—
Glucosamine HCl	—	tr	—	—	tr	tr
Sucrose	—	tr	—	—	2%	1%
Glucurone[a]	—	—	tr	—	—	—
Xylose, pentoses	—	—	tr	—	—	—
Furfural	—	—	tr	—	—	—
5-Ketogluconolactone[b]	—	—	tr	—	—	tr
Galactono-γ-lactone[c]	—	—	tr	—	—	tr
Erythrose	—	—	—	tr	—	1%
Glyceraldehyde	—	—	—	—	—	1%
Oat starch[d]	—	tr	—	—	1%	—
Waxy maize starch	—	tr	—	—	3%	tr
Glycogen[e]	—	tr	—	—	3·5%	tr
Inulin[f]	—	tr	—	—	4·5%	tr
Agar[f]	—	tr	—	—	2%	tr
Cellulose[g]	—	—	—	—	2%	tr
Araboxylan[h]	—	—	tr	—	—	—

* 30–60 mg in 6 ml of HI under reflux for 1 hr.
† expressed as % of wt. of sample taken; *tr* denotes $\geq$ 0·02%.
‡ In addition to the products shown, all compounds in this table gave a trace of CO_2, except for a, b and c, which gave approx. 0·75 mole of CO_2 per mole of compound.
d, Anderson and Greenwood, *J. Sci. Food Agric.*, 1955, **6**, 587.
e, ex Mussel; L. Light and Co. Ltd.
f, B.D.H. Ltd.
g, ex *Nitella translucens;* Anderson and King, in preparation.
h, ex Rye flour; Aspinall and Sturgeon, *J. Chem. Soc.*, 1957, 4469.

TABLE II

Compound*	Volatile products†
Sorbitol, mannitol	CO_2 (tr) + n-hexane (tr) + 2-iodohexane
Ribitol	CO_2 (tr) + n-pentane (tr) + 2-iodopentane
Erythritol	CO_2 (tr) + 2-iodobutane
Glycerol	isopropyl iodide
Ethylene glycol	ethylene + ethyl iodide
Allyl alcohol	isopropyl iodide
Vinyl ethyl ether	ethyl iodide

* Reaction details as in Table 1, footnote †.
† For yields of alkyl iodides, see Discussion: tr denotes $\geq$ 0·02%.

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DISCUSSION

When a carbohydrate material is suspected to have a low methoxyl content, large sample weights must be employed if the methyl iodide released is to be determined accurately. There is also a tendency for reflux periods longer than normal to be used (*cf.* ref. 2). Table III shows that *up to a certain ratio* (100 mg of sample per 6 ml of hydriodic acid) the volatile products from sugars are independent of the sample weight taken: for larger samples, different decomposition mechanisms are clearly

TABLE III

Wt. of glucose, *mg**	Reflux period, *hr*	Volatile products†
20–100	1	CO_2 (tr) + n-hexane (tr) + 2,5-dimethylfuran (2%)
20–100	4	CO_2 (tr) + n-hexane (tr) + 2,5-dimethylfuran (4%)
250	1	CO_2 (tr)
500	1	CO_2 (tr) + methyl iodide (0·12%)
500	3	CO_2 (tr) + methyl iodide (0·4%)

* treated with 6 ml of HI under reflux. † yields expressed as in Table 1.

involved. Hexyl or other iodides are only liberated, however, when hexahydric alcohols are present. This, therefore, refutes the suggestion made by Gran.[2] Table III shows that methyl iodide is only formed when exceptionally large weights of sugars are reacted; the very small amount liberated (equivalent to 0·03% and 0·1% of methoxyl after 1 and 3 hours respectively) does not explain in full the anomalous results previously reported.

Alternative possible sources of error were therefore investigated. Those included (*a*) volatilisation of iodine, (*b*) formation of 2,5-dimethylfuran and of hydrocarbons and acetone, (*c*) retention by polysaccharides of organic solvents used in their preparation.

Volatilisation of iodine

Previous workers[7,8] have commented on the volatilisation of small but significant quantities of iodine. In particular, Belcher[8] showed that volatilisation could occur, although correct results were obtainable if the appropriate increased "blank" value was taken into account. This, however, indicates that iodine vapour, when liberated in quantity, is not *totally* retained by aqueous scrubbers. Our results are in agreement, but the amounts of iodine passing the scrubber are very small, even under testing conditions.

Volatilisation of iodine is therefore not the only possible source of error, although it may well have made a major contribution to some of the high results reported by previous workers, particularly when very large sample weights, fast flow rates and long reflux periods were used. Any tendency for errors to arise through volatilisation of iodine can be minimised by use of the solid scrubber, soda-asbestos.[19]

Result of formation of 2,5-*dimethylfuran*

The observation that 2,5-dimethylfuran is one of the volatile reaction products from certain sugars permits a new explanation of anomalous high results to be given. Soda-asbestos and the scrubbing solutions normally used in the Zeisel determination do not absorb 2,5-dimethylfuran.

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When 100 mg of this compound were added to 10 ml of the conventional oxidising solution (glacial acetic acid/bromine/potassium acetate) used in the iodometric determination of alkyl iodides,[12] a reaction, clearly involving bromine, took place. A precipitate, found to be potassium bromide, was produced. When the determination was completed in the usual way, the thiosulphate titre indicated, when carried out immediately, an apparent addition of 0·9 mg of methyl iodide. If 10 min were allowed to elapse before titrating,[6] the titre was equivalent to 1·8 mg of methyl iodide, indicating 0·4% of methoxyl. Slow liberation of iodine continued for 5 hours, when the apparent methoxyl content was 1·2%. Furan and 2-methylfuran reacted similarly, but liberated smaller quantities of iodine than 2,5-dimethylfuran. The effect of 2,5-dimethylfuran

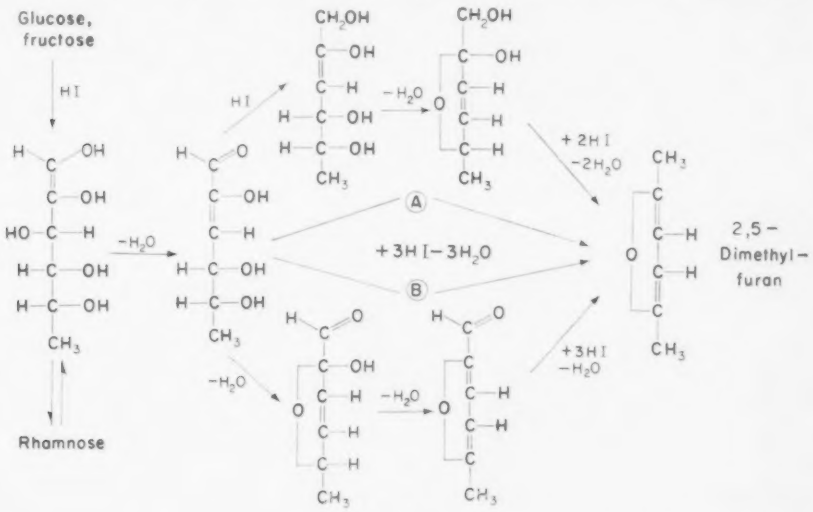

FIG. 1.

was not associated with addition of excess formic acid[20] or excess sodium acetate and sulphuric acid,[21] and clearly contributes to the anomalous Zeisel reactions of sugars.

When furan is added to a cold solution of bromine in acetic acid containing potassium acetate, potassium bromide is precipitated and 2,5-diacetoxy-2,5-dihydrofuran, which is hydrolysed to malealdehyde, is produced in good yield.[22] Our experiments show that both 2-methyl- and 2,5-dimethylfuran react analogously to furan, although 2,5-diacetoxy-2-methyl-5-hydrofuran was too unstable[23,24] to be isolated from the 2-methylfuran reaction mixture. The following facts suggest that the hydrolysis products are involved in the liberation of titratable iodine: (*a*) iodine is released continuously for 4–5 hour, (*b*) the relative instabilities of the diacetoxy addition products increase in the order, furan, 2-methylfuran, 2,5-dimethylfuran, which is the order of increasing yields of iodine by these substances.

Pathway *A* in Fig. 1 shows a possible reaction mechanism for the unexpected formation of 2,5-dimethylfuran. When 5-methylfurfural was refluxed with hydriodic acid, extensive resinification and polymer formation occurred; negligible amounts of 2,5-dimethylfuran were produced. Pathway *B* is therefore not operative. From Tables I and II, it is also apparent that reaction of glucose with hydriodic acid does not involve the intermediate formation of sorbitol.

Quantitative infrared experiments showed that 100 mg of glucose refluxed with hydriodic acid (6 ml) for 1 hour liberated 2 mg of 2,5-dimethylfuran. This, it can be calculated from the results already given, would liberate iodine equivalent to an apparent methoxyl content of 0·01 %. The yields of 2,5-dimethylfuran that are found explain positive errors of the magnitude reported by Adams and Castagne,[1] whose results have been duplicated in experiments using the Vieböck titration.

Result of liberation of hydrocarbons and acetone

The n-hydrocarbons liberated (see Table I) are, like 2,5-dimethylfuran, not retained by the scrubbers normally employed. Pentane, hexane and heptane did not interfere with the Vieböck determination, although a sluggish starch/iodine end-point, caused presumably by slight solvent-extraction of the iodine, was observed.

Table I shows that certain substances liberate small amounts of acetone. Morgan[10] considered that acetone might interfere in Vieböck determinations. The blank values found in experiments using 100 mg of acetone were, however, negligible.

Products from polyhydric alcohols

Table II shows the volatile products given by polyhydric alcohols. Propylene was not produced from glycerol (*cf.* ref. 10). We confirm, however, that the relative amounts of ethylene and ethyl iodide produced from ethylene glycol are affected by several factors;[10] we found that the concentration of phenol used as solubiliser was also critical, and this effect is under investigation. For the present purpose, one mole of ethylene glycol gives 0·4–0·6 mole of ethyl iodide.

In 1 hour, 1 mole of glycerol liberates 0·9–1·0 mole of iso-propyl iodide. The relative involatility ascribed[7,10] to iso-propyl iodide is difficult to understand; even 2-*iodobutane* is sufficiently volatile for approximately 0·8 mole to be given by 1 mole of erythritol in 1 hour. 2-*Iodopentane* and 2-*iodohexane* are less volatile, but the amounts volatilised in 1 hour indicated apparent methoxyl contents of 40% for ribitol and 15% for mannitol. (*cf.* ref. 4).

Formation of vinyl iodide

Von Rudloff's proposal that vinyl iodide was formed from ethylene glycol in the Zeisel reaction was not substantiated. Allyl alcohol gives 1 mole of iso-propyl iodide, whilst vinyl ethyl ether gives 1 mole of ethyl iodide as the only volatile product (see Table II). Vinyl propionate gives no volatile products. The reaction

$$R{\cdot}O{\cdot}CH{:}CH_2 \xrightarrow{H^+} R{\cdot}OH + CH_3CHO$$

(which represents the essential reaction involved in the standard method[25] for analysis of vinyl ethers) explains our findings. Vinyl groups are converted to acetaldehyde, which immediately polymerises so that no volatile products result. Vinyl iodide is therefore not a possible volatile reaction product in Zeisel determinations.

Von Rudloff's proposal[4] was based on the detection of formaldehyde after passage of the volatile products from the reaction of ethylene glycol with HI (*i.e.*, ethylene and ethyl iodide) through a permanganate-periodate reagent. Tests show that this oxidising reagent produces some formaldehyde from ethylene; there is therefore no need to postulate formation of vinyl iodide in order to explain the production of formaldehyde.

CONCLUSIONS

It is evident that several factors can contribute to cause anomalous results. Samples should not be larger than required to give the minimal amount of methyl iodide determinable. The reflux period should not be longer than normal; true methoxyl compounds react within 8–12 minutes,[7,9,13,26] and it is suggested that reflux of carbohydrate materials for longer than 1 hour leads only to increased error. High results from volatilisation of iodine can be eliminated by using the soda-asbestos scrubber.[9,19] Small positive errors of the magnitude reported by Adams and Castagne[1] are given in the Vieböck procedure; these are caused by the production of 2,5-dimethylfuran.

The larger errors reported by certain authors (*cf.* refs. 1,2) cannot be explained by the 2,5-dimethylfuran contribution alone; two suggestions can be offered. Firstly, that abnormally large samples were allowed to react for excessive periods, so creating errors through liberation of 2,5-dimethylfuran and volatilisation of iodine; and possibly also, in extreme cases, through formation of methyl iodide. Secondly, that the polysaccharide samples concerned retained small amounts of organic solvents, particularly alcohols, ethers or esters used in their preparation or isolation. Jansen[27] warned that pectic materials were particularly liable to give this effect; the warning has been repeated more recently[28] with regard to wood products. Experiments[29] have shown that organic solvents used to de-fat or dehydrate polysaccharide materials are retained, up to temperatures at which the materials begin to decompose, despite oven and high-vacuum drying at temperatures much higher than the boiling-point of the solvents involved (*cf.* ref. 27). Although pectic materials and plant gums gave the greatest retention, starches retained smaller but easily measurable quantities (*cf.* ref. 30).

Polysaccharide materials isolated with the aid of organic solvents should therefore be re-dissolved, dialysed and freeze-dried wherever possible, otherwise misleading results will be given in alkoxyl and other analyses: care should still be taken with freeze-dried samples, which can retain solvents.[31] When freeze-drying is not possible, the use of methanol and methoxy compounds should be avoided; analysis by one of the valid methods[15,32] for methoxyl in presence of ethoxyl can then be used. For materials suspected to contain both methoxyl and ethoxyl groups, the use of isopropanol or acetone during preparation will allow the infrared method[15] to give the true content of both alkoxyl groups: methoxyl determinations may also be made in the presence of polyhydric alcohols, since none of these (see Table II) liberate methyl iodide. Indeed, examination of the spectrum of the mixture of volatile reaction products would also reveal which polyhydric alcohols, or mixtures thereof, were present, if this were not otherwise known. Valuable evidence in structural studies, in the detection of anomalous linkages, and in the examination of products obtained by periodate oxidation[3] or hydrogenolysis[33] may thus be given by the infrared method, which also offers a rapid method for "difficult" analyses such as the determination of glycerol in presence of residual sugar substrates and 2,3-butanediol.[34]

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Zusammenfassung—Die flüchtigen Reaktionsprodukte, die während der Zeiselbestimmung von Zuckern und ähnlichen Substanzen entstehen, wurden identifiziert. Ein Produkt aus gewöhnlichen Zuckern ist 2,5-Dimethylfuran, welches die Bestimmung von Alkyljodid nach Vieböck stört. Es

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wurde gezeigt, dass diese Substanz dazu beiträgt, dass scheinbare Alkoxylwerte erhalten werden. Die Annahmen, dass Hexyljodid gebildet wird und dass Vinyljodid als Produkte aus Polyalkoholen enstehen, wurde als unzutreffend bewiesen.

Résumé—Les produits de réaction volatiles obtenus dans les dosages de sucres et de composés apparentés par la méthode de Zeisel ont été identifiés. Un de ces produits obtenu à partir de certains sucres courants est le 2,5-dimethylfuranne, qui gêne dans le dosage de l'iodure d'alkyle par la méthode de Viebock; les auteurs ont montré que ce produit était la cause des valeurs apparentes d'alkoxyle. Les suggestions suivantes ont été réfutées: de l'iodure d'hexyle se dégage à partir des sucres, l'iodure de vinyle est un produit obtenu à partir des alcools polyhydriques.

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METALLOCHROMIC INDICATORS—X*

A NEW MIXED INDICATOR FOR CHELATOMETRIC DETERMINATION OF CALCIUM

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Summary—A new mixed indicator for chelatometric determination of calcium, prepared by mixing fluorescein complexone and phenolphthalein complexone in the ratio of 4:1, is described. It has been shown by comparison with fluorescein complexone alone that in chelatometric titrations of calcium in pure solution and in the presence of sodium salts this mixed indicator gives a sharper end-point and a more accurate recovery of calcium.

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IN a previous communication of this series,[1] the properties of phenolphthalein complexone have been described, the reaction of which with calcium is especially notable: at lower pH (10–11) calcium ions cause a colour change from pink to red; in more alkaline solution (pH 13–14), where the indicator is itself coloured intense purple, an almost complete discoloration takes place on addition of calcium. On titration with EDTA the original colour returns.[1] This diverse behaviour of phenolphthalein complexone toward calcium ions in different pH ranges has been explained by assuming differences in the nature of the bond between the phenolic oxygen of the indicator and the cation; it is postulated that at lower pH values the bond has an ionic character, while at higher pH it is predominantly covalent.[2,3]

The possibility of the practical application of phenolphthalein complexone as an indicator in chelatometric titrations of calcium has not been studied in detail so far, since in preliminary experiments it did not appear promising in comparison with other more suitable "complexan-type" indicators. The end-point colour change at higher pH has not been found sufficiently sharp for practical purposes. However, interesting phenomena have been observed[2] when using phenolphthalein complexone in mixture with fluorescein complexone (Calcein, Fluorexon).[4] At a suitable ratio of these dyes, the pink colour of the calcium complex of phenolphthalein complexone is screened by the intense green fluorescence of fluorescein complexone. On the other hand, at the equivalence point, the purple colour of the free phenolphthalein complexone fully obscures the residual fluorescence of fluorescein complexone. Hence, this combination represents a unique case where the disadvantages of both indicators are mutually corrected. For this reason, this combination has now been examined in detail in order to find the most advantageous ratio of the indicators; the application of the resulting mixed indicator to the chelatometric determination of calcium led to an improvement in the end-point change and to an objective increase of accuracy as compared with fluorescein complexone when used alone.

* Part IX: See *Coll. Czech. Chem. Comm.*, 1960, **25**, 1037.

EXPERIMENTAL

Reagents

EDTA solution, 0·025M: Prepared by dissolving 18·62 g of disodium dihydrogen ethylenediaminetetra-acetate in water and diluting to 2000 ml. The solution was standardised in the usual manner.

Calcium solution, 5 mg Ca^{2+}/1 ml: Prepared from A.R. calcium nitrate. Its titre was checked by chelatometric titration with methylthymol blue, thymolphthalein complexone and cresolphthalein complexone, respectively, as indicators.

Fluorescein complexone (Fluorexon Lachema) and phenolphthalein complexone (Fenolftalexon Lachema) were used as 1:100 finely ground mixtures with potassium chloride.

Procedure

To a sample of calcium salt diluted with water, 2 ml of 5*N* potassium hydroxide were added. The volume was made up to 100 ml with water, indicator was added, and the solution was titrated with 0·025*M* EDTA solution to the quenching of the brilliant green fluorescence (in the case of fluorescein complexone alone) or to the simultaneous colour change from pale yellow to purple-red. All titrations were carried out in diffuse daylight.

RESULTS

Titrations with fluorescein complexone

The quality of the fluorescent end-point of this indicator, and also the accuracy of the determination of calcium in pure solution, are proportional to the amount of calcium to be titrated. With an increasing amount, the end-point is less sharp and the results of individual determinations are scattered over a larger interval. The errors in the recovery of calcium are predominantly negative and the standard deviation shows an increasing tendency.

In the presence of larger amounts of sodium (added as sodium chloride), the sharpness of the end-point is affected by the relatively strong residual fluorescence (*cf.* reference 5). The average recovery of calcium appears to be slightly high, and the reproducibility of the results obtained decreases, as deduced from the values of standard deviations.

The results of all titrations with fluorescein complexone as indicator are given in Table I.

TABLE I.—TITRATION WITH FLUORESCEIN COMPLEXONE AS INDICATOR

Ca taken, *mg*	Na added, *mg*	Ca found, *mg*	Standard deviation	Number of detms.
5·00	—	5·01	±0·016	10
10·00	—	9·99	±0·039	15
24·99	—	24·97	±0·048	10
49·99	—	49·96	±0·056	10
10·00	200	10·03	±0·045	15
10·00	500	10·02	±0·073	15

Titrations with the mixed indicator

In order to establish the optimum ratio of the indicators, preliminary experiments have been made with fluorescein complexone—phenolphthalein complexone mixtures in ratios ranging from 6:1 to 1:1. The best fluorescent and colour end-point with regard to sharpness has been observed when using this mixture in a ratio of 4:1, and the titrations with this mixed indicator have given the most accurate and reproducible recoveries of calcium.

In comparison with fluorescein complexone alone, the determination with this mixed indicator gives a more regular distribution of the results around the theoretical value and the standard deviation remains practically constant, even with calcium amounts up to 50 mg. When sodium is present in a 20–50-fold excess, the end-point change remains sharp, since the disturbing influence of the residual fluorescence is negligible. Although the results show a slight tendency for higher recoveries of calcium in this case also, the accuracy of the determination is not unfavourably affected by the presence of sodium (see Table II).

TABLE II.—TITRATION WITH THE MIXED INDICATOR

Ca taken, *mg*	Na added, *mg*	Ca found, *mg*	Standard deviation	Number of detms.
5·00	—	5·01	±0·024	10
10·00	—	10·01	±0·025	15
24·99	—	24·98	±0·021	10
49·99	—	49·97	±0·027	10
10·00	200	10·00	±0·014	15
10·00	500	10·02	±0·034	15

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DISCUSSION

Fluorescein complexone is one of the best chelatometric indicators for the determination of calcium. Nevertheless, further improvement has been achieved by combining it with phenolphthalein complexone. This combination has a sound theoretical basis since it provides a mutual correction of disadvantages of the two indicators. The new mixed indicator is especially suitable for the chelatometric determination of calcium in the presence of sodium salts, where fluorescein complexone alone gives only a poor fluorescent end-point change.[5]

In respect of interferences of other cations, the proposed mixed indicator has the drawbacks of both of its components. In spite of this fact, we believe that the mixed indicator will find valuable applications in those cases where the determination of calcium is preceded by its separation from other interfering elements.

It is true that one of the tendencies of modern analytical chemistry is the search for new methods of determination of a given cation even in complex mixtures. However, there also exists a simultaneous development of modern separatory methods which justify the elaboration of procedures for determining individual cations in pure solutions. In such cases, the proposed mixed indicator allows the most accurate determination of calcium known so far.

Zusammenfassung—Ein neuer Indikator für die chelatometrische Bestimmung von Calzium, hergestellt durch Zusammenmischen von Fluoresceinkomplexon und Phenolphthaleinkomplexon im Verhältnis 4:1, wurde beschrieben. In Vergleichsversuchen mit Fluoresceinkomplexone allein wurde gezeigt, dass bei der Titration von Calzium in reiner Lösung oder in Anwesenheit vom Natriumsalzen, der beschriebene Mischindikator einen schärferen Endpunkt sowie genauere Resultate gibt.

Résumé—Les auteurs ont décrit un nouvel indicateur mixte pour le dosage complexométrique du calcium; cet indicateur est préparé en mélangeant du fluorescéine-complexone et du phénolphtaléine-complexone dans le rapport 4/1. Les auteurs ont montré, par comparaison avec le

fluoresceine-complexone seul, que, dans les titrages complexométriques du calcium en solution pure et en présence de sels de sodium, cet indicateur mixte donnait un point équivalent plus net et une détermination plus précise du calcium.

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NEW SELECTIVE MICROMETHODS IN THE ANALYSIS OF METALS

TITRIMETRIC DETERMINATION OF SMALL AMOUNTS OF NICKEL AT AN EQUIVALENT RATIO OF 1:24

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Summary—A new selective titrimetric method for the determination of minute amounts (75 to 250 μg) of nickel has been evolved. Nickel is precipitated as nickel dimethylglyoxime. The washed precipitate is dissolved in 20% hydrochloric acid and hydrolysed, producing an equivalent amount of hydroxylamine. The hydroxylamine content is determined in the hydrolysate by oxidation with bromine chloride, being converted to nitric acid. The equivalent weight of nickel in the method corresponds to 1/24 of the atomic weight.

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THE analytical methods evolved for the determination of nickel ions on the basis of the formation of a precipitate of nickel dimethylglyoxime practically insoluble in water[1] are extremely selective. In addition to nickel^{II} ions, only palladium^{II} ions are capable of forming a precipitate with dimethylglyoxime. The former can be precipitated quantitatively in an ammoniacal solution (or one buffered by acetate), while the precipitation of the latter requires a medium slightly acidified by hydrochloric acid; palladium dimethylglyoxime is readily dissolved in ammonia. Thus it is possible to separate nickel from palladium by altering the pH value of the reaction mixture. The coloured complexes of dimethylglyoxime with iron^{II}, cobalt^{II} and copper^{II} ions are soluble in water, and they only interfere with the quantitative precipitation of nickel in very high concentrations.

Many papers[2] deal with the practical application and selectivity of the analytical methods based on the formation of nickel dimethylglyoxime. The majority of these methods are gravimetric ones. It is also possible to determine amounts of nickel from 0·01 to 0·1 mg by photometry,[3] using the water-soluble coloured complex of dimethylglyoxime formed with nickel^{IV} ions. By using an ethanolic solution of dimethylglyoxime, nickel^{II} ions can be titrated directly, with instrumental indication of the end-point (usually by amperometry).[4]

Tougarinoff,[5] and Furman and Flagg[6] dissolved the filtered and washed precipitate of nickel dimethylglyoxime in acid. By boiling with acid the dimethylglyoxime was hydrolysed to the corresponding ketone and hydroxylamine, the latter being determined by oxidimetry. Tougarinoff[5] oxidised the hydroxylamine with a solution of iron^{III} to nitrous oxide, and measured by permanganometry the amount of iron^{II} ions formed. In this method, the equivalent weight of nickel corresponds to 1/4 of the atomic weight (A/4). Furman and Flagg,[6] on the other hand, oxidised hydroxylamine with bromate to nitric acid, and in this case the equivalent weight of nickel corresponds to 1/24 of the atomic weight (A/24). However, they reported (and this is in accordance with our own observations) that this method can only be used on a 0·1*N* scale. Errors of

±4–5% may occur when the consumption of the standard solution is below 10 ml, satisfactory results only being obtained when the consumption of standard solution is more than 20 ml (equivalent to 5–10 mg of nickel). As a consequence, the advantage of operating with a low equivalent weight is practically lost.

In an earlier communication[7] a method for the determination of hydroxylamine, based on its oxidation by bromine chloride, was suggested. This reaction takes place according to the equation

$$NH_2OH + 3BrCl + 2H_2O = HNO_3 + 3HBr + 3HCl \qquad (1)$$

It was found that this oxidation also was suitable for the measurement of hydroxylamine on a 0·01*N* scale.

Because of the low solubility of nickel dimethylglyoxime, the reaction was utilised for the titrimetric determination of minute amounts of nickel, after dissolving the precipitate in hydrochloric acid, and hydrolysing dimethylglyoxime to hydroxylamine and the corresponding ketone (and to the decomposition products of the latter).

Since one nickel atom forms a precipitate with two molecules of dimethylglyoxime, and two molecules of hydroxylamine are derived from each molecule of dimethylglyoxime, and since in the oxidation of hydroxylamine by bromine chloride the change in the oxidation state of the nitrogen atom is 6 ($-I \rightarrow +V$), the equivalent weight of nickel in this method of determination is 1/24 of the atomic weight (A/24). Therefore 1 ml of 0·01*N* BrCl is equivalent to 24·45 μg of nickel.

The selectivity of this method is dependent on that of the formation of nickel dimethylglyoxime precipitate. It is therefore possible to determine small amounts of nickel in the presence of almost any other metal.

EXPERIMENTAL

(1) *Decomposition of hydroxylamine on boiling in a medium of* 20% *hydrochloric acid*

Hydroxylammonium chloride suffers a partial decomposition on boiling in a solution of 20% hydrochloric acid for more than 10 min. The content of hydroxylamine was determined by oxidation with bromine chloride. Since oxygen dissolved in the reaction mixture would interfere strongly in the iodometric measurement, because of the strongly acidic medium, 0·5–1·0 g of potassium hydrogen carbonate was added to the cooled solution, after boiling with hydrochloric acid.

(2) *Hydrolysis of dimethylglyoxime*

On boiling dimethylglyoxime on a 0·1*N* or 0·01*N* scale for 1 min, it quantitatively hydrolyses to hydroxylamine and the corresponding ketone (and to the decomposition products of the latter).

(3) *Titrimetric determination of nickel*

Reagents:

Bromate-bromide solution: 0·01*N* solution (1:2 ratio of bromate to bromide), prepared by weighing 0·2784 g of potassium bromate and 0·3967 g of potassium bromide, dissolving in distilled water and making the volume to 1000·0 ml.

Sodium thiosulphate: 0·01*N* standard solution.

Dimethylglyoxime: 1% ethanolic solution.

Nickel dimethylglyoxime: cold saturated aqueous solution.

Hydrochloric acid solution: 20% (azeotropic).

Ammonium hydroxide solution: 2*N*

Potassium iodide

Starch solution: 1% (decomposed and preserved by 0·1% salicylic acid).

All the reagents should be of analytical grade.

Method

An aliquot of the stock solution (not more than 5 ml) containing 75–250 μg of nickel, is transferred to a 25-ml beaker, and while boiling, 0·2 ml of dimethylglyoxime solution and 1 ml ammonium hydroxide solution are added dropwise. Boiling is continued for about 5 min, the solution is cooled for 10 min, and the liquid together with the precipitate is poured on to a G3 glass filter and the mother liquor is sucked off. The residual precipitate in the beaker, together with the precipitate on the filter are washed with 2 × 6 ml of hot nickel dimethylglyoxime solution, and then with 5 ml of water. The washed precipitate is dissolved in 6 ml of hot hydrochloric acid, the beaker and the filter are washed with a further 2 × 6 ml of hydrochloric acid, and the hydrochloric acid solution is collected in a 100-ml beaker. The solution is boiled for 1 min, allowed to cool for 10 min, quantitatively washed into a Schulek bromination flask, and diluted with water to 100–150 ml. In order to eliminate the interfering effect of oxygen dissolved in the reaction mixture, about 0·5 g of potassium hydrogen carbonate is added to the solution. (If a greater amount of hydrochloric acid was necessary for dissolving the precipitate, a consequently greater amount of potassium hydrogen carbonate is obviously necessary). Sufficient 0·01*N* standard solution is transferred to the flask to maintain an excess of over 100% of bromine chloride* formed by the hydrochloric acid.

TABLE I.—DETERMINATION OF NICKEL ON 0·01*N* SCALE

Ni weighed, μg	Total 0·01*N* BrCl *ml*	0·01*N* $Na_2S_2O_3$ consumed, *ml*	0·01*N* BrCl consumed, *ml*	Ni found, μg	Δ, μg	Δ, %
80·04	9·96	6·75	3·21	78·48	−1·56	−1·95
80·04	20·00	16·76	3·24	79·22	−0·82	−1·02
135·0	20·00	14·54	5·46	133·5	−1·5	−1·11
135·0	20·00	14·59	5·41	132·3	−2·7	−2·0
271·6	29·96	18·96	11·00	269·0	−2·6	−0·96
271·6	29·96	18·94	11·02	269·4	−2·2	−0·81

The flask is closed by the moistened attachment equipped with a tap. After standing for 15 min, the flask is cooled with tap water (a vacuum forms), and 10 ml of freshly prepared 5% solution of potassium iodide are introduced into the reaction mixture through the tap and the attachment. The liberated iodine is then immediately titrated with 0·01*N* sodium thiosulphate with starch as indicator.

1 ml of 0·01*N* BrCl ≡ 24·45 μg of nickel (log 38828).

The error of the method ranges from −1 to −2% (Table I). This negative error on the 0·01*N* scale

TABLE II.—DETERMINATION OF NICKEL ON 0·1*N* SCALE

Ni weighed, *mg*	Total 0·1*N* BrCl, *ml*	0·1*N* $Na_2S_2O_3$ consumed, *ml*	0·1*N* BrCl consumed, *ml*	Ni found, *mg*	Δ, *mg*	Δ, %
0·8004	9·96	6·69	3·27	0·7995	−0·0009	−0·11
0·8004	20·00	16·75	3·25	0·7946	−0·0058	−0·72
1·350	20·00	14·50	5·50	1·345	−0·005	−0·37
2·716	29·96	18·77	11·19	2·736	+0·020	+0·74
2·716	29·96	18·80	11·16	2·723	+0·007	+0·26

* Through the effect of hydrochloric acid, bromine chloride develops from the standard solution according to the equation:

$$BrO_3^- + 2\ Br^- + 3\ Cl^- + 6\ H^+ = 3\ BrCl + 3\ H_2O$$

(75 to 250 μg Ni) arises from the solubility of the precipitate proper, and is no longer invariably negative on the 0·1*N* scale (0·75 to 2·5 mg Ni):

For the determination on the 0·1*N* scale, the procedure is as follows:

Precipitation is carried out in a volume not exceeding 10 ml using 2 ml of dimethylglyoxime solution. In order to adjust to the required pH value, 2 ml of ammonium hydroxide solution are added to the neutral solution. A period of 5 min is necessary for the oxidation of hydroxylamine by bromine chloride. Otherwise the determination is conducted as previously described.

1 ml of 0·1*N* BrCl = 0·2445 mg of nickel (log 38828).

The error of the method is in the range of $\pm 1\%$ (Table II).

Zusammenfassung—Ein neues selektives Verfahren wurde zur Bestimmung von sehr kleinen Mengen Nickel (75–250 μg) ausgearbeitet. Nickel wird als Nickeldimethylglyoxim gefällt. Der ausgewaschene Niederschlag wird in Salzsäure (20%) aufgelöst und hydrolytisch gespallten, wobei sich äquivalente Menge Hydroxylamin bildet. Der Hydroxylamingehalt der Lösung wird durch Oxydation (zu Salpetersäure) mittels Bromchloride bestimmt. Das Äquivalentgewicht des Nickels beträgt 1/24 des Atomgewichtes.

Résumé—L'auteur a développé une nouvelle méthode titrimétrique sélective de dosage de faibles quantités de nickel (75–250 μg). Le nickel est précipité à l'état de diméthylglyoxime de nickel. Le précipité lavé est dissous dans de l'acide chlorhydrique à 20 pour cent et est hydrolysé formant une quantité équivalente d'hydroxylamine. La teneur en hydroxylamine est mesurée dans l'hydrolysat par oxydation par du chlorure de brome (en donnant de l'acide nitrique). Le poids équivalent de nickel dans cette méthode correspond à 1/24 du poids atomique.

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SPOT TEST DETECTION AND COLORIMETRIC DETERMINATION OF ANILINE, NAPHTHYLAMINE AND ANTHRAMINE DERIVATIVES WITH 4-AZOBENZENEDIAZONIUM FLUOBORATE

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Summary—Some new sensitive procedures are introduced for the detection and determination of aniline, α- and β-naphthylamines, and α- and β-anthramines, as well as their *N*-alkyl and *N,N*-dialkyl derivatives. The chromogens are (*p*-phenylazophenylazo)-aniline, -naphthylamine and -anthramine dyes. For example with *N,N*-dimethylaniline, the blue di-cation of *N,N*-dimethyl-*p*-(*p*-phenylazophenylazo)aniline is formed. The absorptivity of *N,N*-dimethylaniline obtained in the colorimetric procedure is 0·823 μg^{-1} ml cm^{-1}. In the analysis for *N,N*-dimethylaniline, Beer's Law was obeyed from 0·1 to at least 3·6 μg per ml of final solution. Because of the widely differing rates of reaction, naphthylamine or anthramine derivatives can be determined in the presence of aniline derivatives. Also, with the help of a masking agent a dialkylaniline can be determined in the presence of primary and secondary amines. Spot tests for aniline, naphthylamine and anthramine derivatives are described, but their sensitivity does not compare with the sensitivities obtained in the colorimetric procedure.

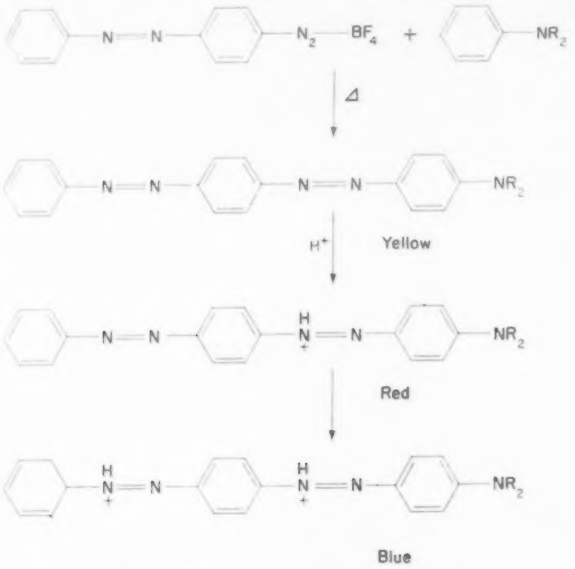
INTRODUCTION

As a result of our expanding industrialisation, various types of aniline derivatives have been introduced into the human environment. Many of these compounds have been shown to have toxic properties; threshold limits for aniline, *N,N*-dimethylaniline and *o*-toluidine have been placed[1] at 5 ppm. Consequently, it was desirable to develop methods of analysis for aniline derivatives. Colorimetric procedures for aniline[2–4] and for polycyclic aromatic primary amines[4] are available in the literature. Several methods for the determination of aniline and *N,N*-dimethylaniline in the air have been described.[5,6] Although these methods are fairly sensitive, they have never been thoroughly evaluated, and are less sensitive and more complicated than the 4-azobenzenediazonium fluoborate procedure.

The use of diazotisation in the determination of aromatic amines has been known for a long time.[7] The method involves the reaction of a diazotised aromatic amine with an aromatic amine coupling agent. In the determination of sulphanilamide through diazotisation and coupling with *H*-1-naphthylethylene-diamine, the final chromogen absorbs[8] at 545 mμ with a molar absorptivity of 51,500. The chromogen obtained in the colorimetric determination of *N*-phenyl-1-naphthylamine with *p*-nitrobenzenediazonium chloride absorbs[9] at 555 mμ with a molar absorptivity of 37,000.

In this paper a new and more sensitive diazotisation method for the determination of several types of aromatic amines is introduced. Some simple spot tests are also described.

The mechanism of the reaction as applied to *N,N*-dimethylaniline is as follows:



The compound is analysed at the blue stage because of the more intense colour of the di-cation as compared to the mono-cation.[10]

In a solvent containing 30 ml of 2-methoxyethanol diluted to 100 ml with concentrated hydrochloric acid, the pure dye absorbed at 632 mμ, as did the solution obtained in the colorimetric determination of *N,N*-dimethylaniline. At this wavelength maximum, the latter solution had a molar absorptivity of 100,000 as compared to 100,000 obtained for the pure dye. These results indicate that a 100% yield of chromogen is obtained in the determination of *N,N*-dimethylaniline.

EXPERIMENTAL

Reagents and apparatus

4-Azobenzenediazonium fluoborate was prepared from 4-aminoazobenzene.[4] A solution of 0·1% of 4-azobenzenediazonium fluoborate in 2-methoxyethanol was used as the reagent in the analytical work. All organic nitrogen compounds were obtained from commerical sources and were purified by crystallisation to a constant melting point or by distillation.

A Cary Model 11 recording spectrophotometer with 1-cm cells was used in the colorimetric determination of aniline derivatives.

Microtube procedure

To 1 drop of the 2-methoxyethanol test solution were added 2 drops of 0·1% 4-azobenzenediazonium fluoborate. The tube was then heated in a boiling water bath for 6 min. Then 2 drops of concentrated hydrochloric acid were added. Because of the reagent's interfering yellow colour at low concentrations of test compound, a blank is advisable in doubtful cases. Colours and limits of identification are given in Table I.

Spot paper procedure

To 1 drop of the 2-methoxyethanol test solution spotted on paper were added 2 drops of 0·1% 4-azobenzenediazonium fluoborate. The spot was treated with a jet of steam for 30 sec and then with a jet of hydrogen chloride gas. Instead of the gas, a drop of concentrated hydrochloric may be placed

TABLE I.—COLORIMETRIC AND SPOT TEST RESULTS OBTAINED IN THE ANALYSIS FOR PHENYL-, NAPHTHYL- AND ANTHRYL-AMINES WITH 4-AZOBENZENEDIAZONIUM FLUOBORATE

Compounds	Colorimetric		Spot tests, ident. limit, μg			
	λ max., $m\mu$	$\varepsilon \times 10^{-3}$	Colour[a]	Microtube	Colour	Paper
Aniline	610	8	V	7	V	7
o-Methylthioaniline	610	9	B	9	B	9
o-Toluidine	618	23	V	15	V	4
o-Anisidine	626	48	V	9	V	2
m-Toluidine	612	63	R	4	B	2
N-Methylaniline	623	65	V	8	V	8
N-Ethylaniline	623	73	B	9	B	9
N-*n*-Propylaniline	623	85	RV	10	V	17
N,*N*-Dimethylaniline	632	100	B	1	B	17
N-Methyl-*N*-ethylaniline	633	80	B	5	B	17
N,*N*-Diethylaniline	635	72	B	5	B	11
N-Allyl-*N*-methylaniline	632	83	B	5	B	11
N-Benzyl-*N*-methylaniline	640	73	V	4	B	14
N,*N*-Di-*n*-propylaniline	637	82	B	6	B	13
N,*N*-Dimethyl-*m*-toluidine	630	120	B	5	B	0.6
α-Naphthylamine[b]	642	95	B	1	B	0·6
N-Methyl-α-naphthylamine[b]	645	99	B	18	B	0·7
N-Ethyl-α-naphthylamine[b]	645	99	B	3	B	0·8
N-1-Naphthylethylenediamine[b]	656	100	B	3	B	0·8
N,*N*-Dimethyl-α-naphthylamine[b]	642	22	B	2	B	2
β-Naphthylamine[b]	603	32	B	10	B	3
α-Anthramine[b]	675	42	G[c]	14	B	2
β-Anthramine[b]	625	56	G[c]	7	V	0·9

[a] B = blue; G = green; V = violet; R = red. Colour of product in microtube changes to green if concentrations of amine falls below ~ 10–40 μg.

[b] The standard colorimetric procedure was followed except that 10 min of standing at room temperature was substituted for the 6 min of heat on the water bath. In the standard colorimetric procedure involving heat the following wavelength maxima and molar absorptivities were obtained α-naphthylamine, 610 (41,000); β-naphthylamine, 605 (57,000); α-anthramine, 544 (28,000); and β-anthramine, 623 (44,000).

[c] Colour obtained without heat or acid for α-anthramine is blue and identification limit is 7 μg; for β-anthramine it is violet with identification limit of 7 μg.

on the paper. However, the sensitivities are lower in the latter procedure because of diffusion. Colours and limits of identification are given in Table I.

Colorimetric procedure

To 5 ml of the 2-methoxyethanol test solution in a 50-ml volumetric flask were added 10 ml of 0·1% 4-azobenzene diazonium fluoborate. The mixture was heated for 6 min in a boiling water bath. It was cooled with an ice water bath, and then diluted to the mark with concentrated hydrochloric acid while cooling to room temperature. The absorption spectrum was then immediately determined. The wavelength maxima and molar absorptivities obtained for different aniline derivatives are given in Table I.

DISCUSSION

Qualitative tests

Two modifications of the spot test procedure are introduced in this paper. A blank must be run in conjunction with the test, especially in the microtube method, at concentrations near the identification limit. This is because the blank has a deep yellow colour and the presence of a small amount of blue chromogen would then give

the test solution a yellow-green colour. This interference could cause difficulty. α-Anthramine is characterised by the fact that it gives a blue colour in the microtube method without any hydrochloric acid. Neither the aniline nor naphthylamine derivatives do this.

Colorimetric procedure

The method introduced in this paper for the determination of *N,N*-dimethylaniline has a very high sensitivity potential for colorimetric analysis.

Other *N*-alkyl and *N,N*-dialkyl anilines give colours of differing intensity. This variation in intensity is mainly due to the varying yields of bisazo dyes obtained in the colorimetric procedure. A slower rate of reaction could have a drastic effect on the yield. In many cases the presence of an orange to red di-cationic tautomer (involving salt formation at an azo nitrogen and the amino nitrogen) also helps to decrease the intensity of the blue colour of the bisazo dye di-cation.[10]

Of the aromatic amines investigated, the ring-substituted aniline derivatives, *N,N*-dimethyl-α-naphthylamine and β-naphthylamine gave the lowest intensities. *m*-Toluidine and *N,N*-dimethyl-*m*-toluidine gave the highest relative intensities, mainly because of the electron donor effect of the *m*-methyl group of the toluidine in the final azo dye.

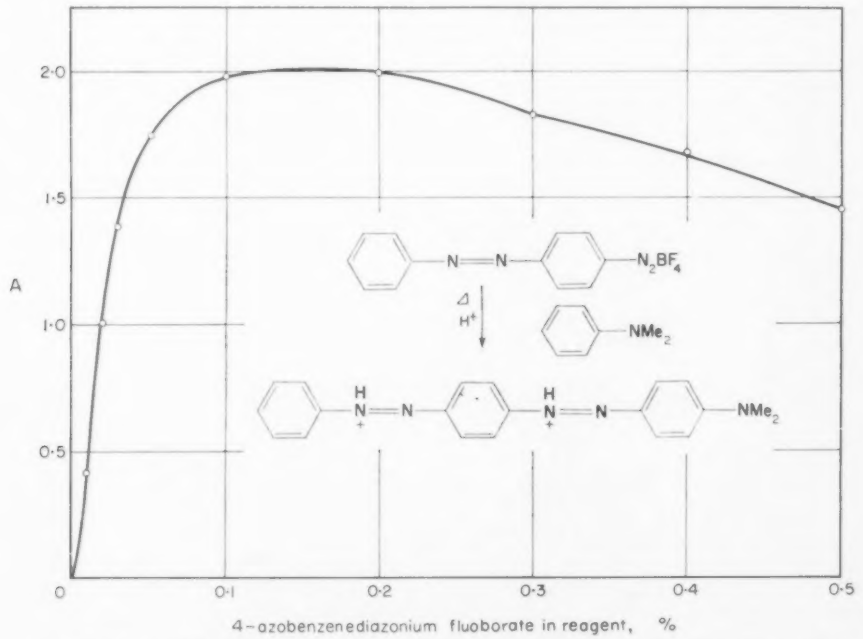


FIG. 1.—Effect of concentration of azobenzenediazonium fluoborate in the reagent solution on the absorbance obtained in the standard colorimetric procedure with *N,N*-dimethylaniline (2×10^{-5} *M*) at λ_{max}. 632 mμ.

While aniline derivatives reacted readily with the reagent only at the boiling point of water, the naphthylamines and anthramines reacted at room temperature (Table I). After the reaction of anthramine and reagent at room temperature, dilution with

2-methoxyethanol to 50 ml gave a purple solution absorbing at 566 mμ with a molar absorptivity of 20,000. These diverse reactions at room temperature and at the boiling point of water should be of value in characterising some of the amines.

The colorimetric procedure has been developed so as to give optimum results with *N,N*-dimethylaniline; in this case a 100% yield of the blue bisazo dye dication was obtained. With proper modification of the standard colorimetric procedure, more intense colours could probably also be obtained for the other aromatic amines. This improvement with modification of conditions has been shown for the α-naphthylamines.

Variables affecting the standard colorimetric procedure for *N,N*-dimethylaniline were investigated. Optimum results were obtained with 0.1% to approximately 0.2% of the reagent (Fig. 1). However, the blank was fairly dark, so 0.1% concentration was chosen as giving the best all-around results. When the reagent and the *N,N*-dimethylaniline test solution were heated in a boiling water bath, it took 6 minutes of heating to obtain the maximum intensity (Fig. 2). Shorter periods of heat had a

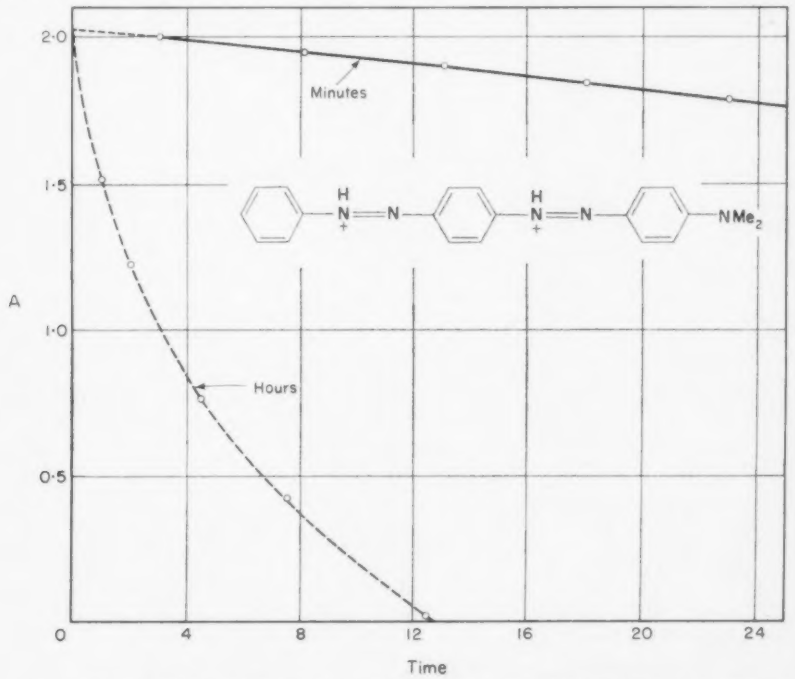


FIG. 2.—The effect on the absorbance at λ_{max} 632 mμ of the heating time at 100° of the reagent and *N,N*-dimethylaniline in the colorimetric procedure. Final concentration of *N,N*-dimethylaniline — 2×10^{-5} *M*.

drastic effect on the intensity; longer periods had a slight effect. The stability of the colour was also investigated (Fig. 3). The absorbance decreased gradually at a steady rate. Readings were preferably taken on a fresh solution, or at least, within a few minutes after the acid was added. The colour obtained in the determination of *N,N*-dimethylaniline was found to obey Beer's Law from 5 μg to at least 180 μg per 50 ml of final solution.

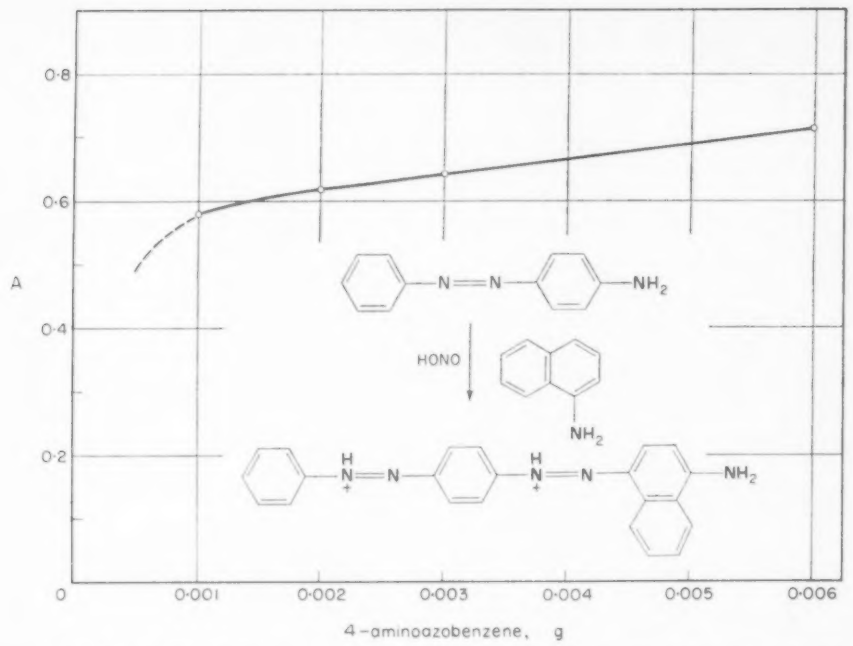


FIG. 3.—Change of absorbance with time at λ_{max} 632 mμ of the final solution obtained with *N,N*-dimethylaniline (2×10^{-5} *M*) in the standard colorimetric procedure.

Decreased reactivity due to substituents

Some aniline derivatives gave a very weak to negligible colour in the standard colorimetric procedure. In compounds such as the nitroanilines, *o*-chloroaniline, *N,N*-dimethyl-*m*-aminobenzoic acid, *N,N*-dimethyl-*p*-bromaniline, *N,N*-dimethyl-*p*-aminobenzaldehyde, the *N,N*-dimethyl nitroanilines and *N,N*-dimethyl-*p*-toluidine, the presence of an electronegative group or a group *para* to the amino group had an adverse effect on the activity. In *N,N*-dimethyl-*o*-toluidine the low order of reactivity is due to the strong steric effect of the *o*-methyl group.[11] This effect forces the dimethylamino group out of the plane of the molecule and as a result causes a low yield of the bisazo dye di-cation.

Interferences

A few diphenylamines and heterocyclic imines were tested by the standard colorimetric procedure. *N*-Methyl-diphenylamine and diphenylamine gave bands at 640 mμ with molar absorptivities of approximately 13,000 and 17,000, respectively. Indole and carbazole gave bands at 560 and 605 mμ with molar absorptivities of 11,000 and 6,000, respectively. Because of their relatively weak basicity, diphenylamines, indoles and carbazoles can be readily separated from the more basic aromatic amines. In this way, aniline derivatives could be determined in the presence of these compounds.

Phenols could be expected to react with the reagent. In the standard colorimetric procedure, phenol itself gave an orange solution which had negligible absorption near

600 mμ. α-Naphthol gave a band at 625 mμ with a molar absorptivity of 7,000. If necessary, phenols could be separated by alkaline extraction.

2,4-Pentadione treated by the standard colorimetric procedure gave a red solution with a band at 535 mμ and a molar absorptivity of 21,000.

Nitromethane, dibutylamine, isobutylamine, formaldehyde and acetone gave negative results.

Acetic anhydride tended to inhibit colour formation.

Determination of α-naphthylamine in a mixture.

A liquid mixture was prepared consisting of 71·5 μg of α-naphthylamine, 930 μg of aniline, 1070 μg of *N*-methylaniline, and 1210 μg of *N,N*-dimethylaniline. Reaction of this mixture in the standard colorimetric procedure (modified by substitution of 10 min of standing at room temperature for 6 min of heating on the water bath) gave an absorption spectrum with maxima at 500 and 642 mμ. The band with a peak at 642 mμ had an absorbance of 0·96. The band with a peak at 500 mμ was mainly derived from aniline and *N*-methylaniline and apparently had little effect on the intensity of the long wavelength band, for 71·5 μg of α-naphthylamine reacted in the same procedure gave a band at 642 mμ with an absorbance of 0·95. The absorbance thus obtained in the mixture corresponds to 70·8 μg of α-naphthylamine which is in excellent agreement with the amount of α-naphthylamine calculated to be present.

Determination of N,N-*dimethylaniline in a mixture*

For the determination of *N,N*-dimethylaniline in the presence of primary and secondary amines, the use of acetic anhydrides as a masking agent was tried. A mixture of 12·1 μg of *N,N*-dimethylaniline and 2 μl of acetic anhydride were heated 10 min, cooled and treated by the standard colorimetric procedure. A molar absorptivity of 78,000 was obtained; without the acetic anhydride the molar absorptivity was 85,000. When a mixture of 12·1 μg of *N,N*-dimethylaniline and 14·3 μg of α-naphthylamine was similarly analysed, a molar absorptivity of 75,000 was obtained for *N,N*-dimethyl aniline, essentially a 96% recovery. When a mixture of 12·1 μg *N,N*-dimethylaniline, 14·3 μg of α-naphthylamine, 10·7 μg of *N*-methyl-aniline, and 9·3 μg of aniline was analysed by the same procedure, a molar absorptivity of 85,000, or a 113% recovery of *N,N*-dimethylaniline, was obtained These results show that the determination of a tertiary amine in the presence of primary and secondary amines with the help of an acylating masking agent is worthy of further investigation.

Zusammenfassung—Einige neue, sensitive Methoden zum Nachweis und zur Bestimmung von Anilin, alpha- und beta-Naphthylaminen, alpha- und beta- Anthraminen sowi deren N-Alkyl-und N,N-Dialkylderivaten werden beschrieben. Die Chromogene sind (p-Phenylazophenylazo)-anilin, -naphthylamin und -anthraminfarbstoffe. Z.B. mit N,N-dimethylanilin wird das blaue Dikation von N,N-dimethyl-p-(p-phenylazophenylazo)-aniline gebildet. Der Absorptionskoeffizient des in der kolorimetrischen Methode erhaltene beträgt 0.83 μg^{-1} ml cm^{-1}. Für N,N-dimethylanilin ist Beers Gesetzt erfüllt im Konzentrationsbereich 0.1 bis mindestens 3·6 μg per ml der fertigen Farblösung. Wegen des sehr grossen Unterschiedes in der Reaktionsgeschwindigkeit können Naphthylamin- und Anthraminderivate in Gegenwart von Anilinderivaten bestimmt werden. Ferner kann durch Einsatz eines Maskierungsmittels ein Dialkylamin in Geganwart von sekundären und primären Aminen bestimmt werden. Tüpfelteste für Anilin-, Naphthylamin- und Anthraminderivate werden beschrieben. Die Empfindlichkeit dieser Nachweise ist jedoch nicht mit der der kolorimetrischen zu vergleichen.

Résumé—Les auteurs ont mis au point de nouvelles techniques sensibles pour déceler et doser l'aniline, les α et β naphtylamines et les α et β anthramines, ainsi que leurs dérivés N-alkyle et N, N-dialkyle. Les chromogènes sont des colorants de la p-phénylazophénylazoaniline, de la p-phénylazophénylazonaphtylamine et de la p-phénylazophénylazoanthramine. Par exemple, avec la N,N-diméthylaniline, le di-cation bleu de la N,N-diméthyl-p-(p-phénylazophénylazo)-aniline est formé. L'absorption de la N,N-dimethylaniline obtenu dans le procèdé colorimétrique est 0,83 g^{-1} ml cm^{-1} Dans l'analyse de la N,N-diméthylaniline, la loi de Beer est suivie de 0,1 à au moins 3,6 μg par ml de solution finale. A cause des vitesses de réaction largement différentes, les dérivés de la

naphtylamine et de l'anthramine peuvent être dosés en présence des dérivés de laniline. Ainsi, à l'aide d'un agent complexant, une dialkylaniline peut être dosée en présence d'amines primaires et secondaires. Des essais par touches sont décrits pour l'aniline, la naphtylamine et l'anthramine, mais leur sensibilité ne se compare pas à celles obtenues dans la méthode colorimétrique.

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THE PRECIPITATION OF NIOBIUM OXINATE OF DEFINITE COMPOSITION

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Summary—Since the composition of niobium oxinate, precipitated from aqueous solution, is apparently not definitely established, several new techniques have been used for the preparation of a compound of definite composition. Of these techniques, homogeneous precipitation of niobium oxinate by means of urea yielded the best results. The product is crystalline and agrees, within the limits of ± 0·5%, with the theoretical formula $NbO(C_9H_6ON)_3$. Furthermore, the solubility in various organic solvents, the spectrum in the ultraviolet and infrared regions, and the electron diffraction have been determined; thermolysis has been carried out; and photomicrographs of the crystals have been taken.

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NIOBIUM oxinate was first described by Süe[1] and the ratio $Nb_2O_5 : 5{\cdot}5C_9H_7ON : 4H_2O$ was proposed for its composition. Methods for its preparation were recently investigated by Doan and Duval[2] who established, on the basis of thermolysis curves, that two moles of oxine were bound to one mole of niobium pentoxide, while the water content varied from experiment to experiment. Szymanski and Archibald[3] found that after heating to 155°, niobium oxinate has the composition $NbO(C_9H_6ON)_3$; however, they left open the question of its composition immediately after the precipitation from an aqueous solution.

Several methods by which it was hoped to improve the conditions for obtaining stoichiometric samples of niobium oxinate from aqueous solutions were tested and can be summarised as follows:

(i) The niobium fluoride complex was decomposed by adding boric acid to a solution containing excess oxine. Precipitation was carried out at pH 3·5, corresponding to that at which the maximum extraction of niobium oxinate in chloroform from an acidic medium[4] was previously obtained by the present authors. This method yielded a voluminous, hardly filterable orange precipitate with 25% of the niobium left in solution.

(ii) In another group of experiments a solution of niobium hydrate was dissolved in dilute hydrofluoric acid and added to an ammoniacal solution of boric acid containing oxine. The concentration of reagents was chosen so as to give, after mixing, a pH of 9·4, equal to the pH at which the maximum extraction of niobium oxinate from an alkaline medium was obtained. The precipitate was greenish-yellow, less voluminous, settled more readily and after successive washings with water, alcohol and ether, gave a product containing a considerable excess of oxine. Two to 4% of the niobium was left unprecipitated.

(iii) A similar product was obtained when ammonium chloride was added to a solution of niobium hydrate in potassium hydroxide to give a pH of 9·2 after final dilution. By this method 85 to 90% of the niobium was recovered.

(iv) The only method which yielded a defined, crystalline product was based on

slow hydrolysis of urea in an acid solution, containing oxalic acid and an excess of the reagent. This method will, therefore, be described in greater detail.

EXPERIMENTAL

Precipitation of defined niobium oxinate

One g of niobium pentoxide was fused with an excess of potassium pyrosulphate, and the cool melt was dissolved in 100 ml of 1*M* oxalic acid[5]. After the addition of 10 ml of concentrated sulphuric acid, and oxine (50% excess), the solution was heated to boiling point. Urea was added in portions approximately five times greater than the theoretical amount, and the solution was diluted to 2000 ml and left in a water bath until it turned brown (pH 7–8). The precipitate obtained by this technique was coarse, crystalline and yellowish-green, and it settled rapidly and was easily washed.

The precipitation was almost quantitative (> 99%). The precipitate was filtered through a sintered-glass crucible, washed with warm water, then with alcohol and ether to speed up drying.

Analysis of the product

Niobium and oxine were determined in all products; precipitates obtained by methods (i) and (ii) were additionally analysed for boron and fluorine.

Niobium was determined by igniting the precipitate at 950° in a porcelain crucible and weighing as niobium pentoxide. The method of Berg[6] was slightly modified for the determination of oxine. The precipitate was dissolved in hydrochloric acid, potassium bromide was added, and the solution was titrated with potassium bromate. The excess of the reagent was reduced by potassium iodide and re-titrated with sodium thiosulphate in the presence of carbon bisulphide. Fluorine was determined by the method of Ballczo and Kaufmann.[7] The sample was dissolved in hydrofluoric acid and distilled, in the presence of perchloric acid, into a solution of sodium hydroxide. Subsequently, the solution was titrated with thorium nitrate using sodium alizarin sulphonate as indicator. Boron was determined spectrographically.

The products prepared by methods (i) and (ii) differ in their water content as well as in the quantity of the absorbed oxine. They were, therefore, dried at 150° before analysis, while the oxinate obtained by method (iv) was only washed with water, alcohol and ether and dried in air. Some samples have been warmed under vacuum at 10^{-4} mm of mercury and 90° in order to sublime the small amounts of oxine, which proved to be negligible.

RESULTS AND DISCUSSION

Table I gives the results of the analyses (a mean value of six precipitations) of oxinate by different methods.

TABLE I.

Method of precipitation	Nb, %*	C_9H_7ON, %*	F, %	B, %
Complexing at pH 3·5	20·9 ± 0·6	72·9 ± 0·2	0·98	0·04
Complexing at pH 9·4	17·1 ± 0·1	80·6 ± 0·5	0·02	0·04
Precipitation from niobate solution	16·5 ± 0·1	81·3 ± 0·2	—	—
Hydrolysis of urea	17·16 ± 0·2	79·74 ± 0·3	—	—

* The theoretical values for niobium and oxine are 17·16 % and 79·88 %, respectively.

The results in the first three horizontal rows were obtained for products dried at 155°, those in the last row for the product dried at room temperature. Only the samples precipitated from an acidic medium by complexing in fluoride solution yielded figures for both components which deviate considerably from theoretical

values. Furthermore, the adsorption of fluoride ions is appreciable, but boron is adsorbed to a much smaller extent.

Owing to the excellent characteristics of the precipitate obtained by the urea method (stoichiometric composition, crystalline nature, rapid settling and low percentage of niobium in the precipitate), this procedure was tested for its applicability to the gravimetric determination of niobium. In a solution labelled before precipitation with radioactive ^{95}Nb, only traces of niobium were detected by radiometric measurements (scintillation counting) in the final filtrate. The method of precipitation was essentially the same as that described above, the only differences being that smaller samples of niobium (50 mg of niobium pentoxide) were taken and the quantities of the reagents were proportionally reduced. Over 99% of niobium pentoxide was recovered in all experiments.

The solution of niobium must be fresh, because if the reagents are added to aged solutions niobic acid is precipitated. It is therefore advisable to decompose the samples immediately before the precipitation.

In order to obtain a thorough characterisation of the product obtained by the hydrolysis method, the following additional measurements were made:

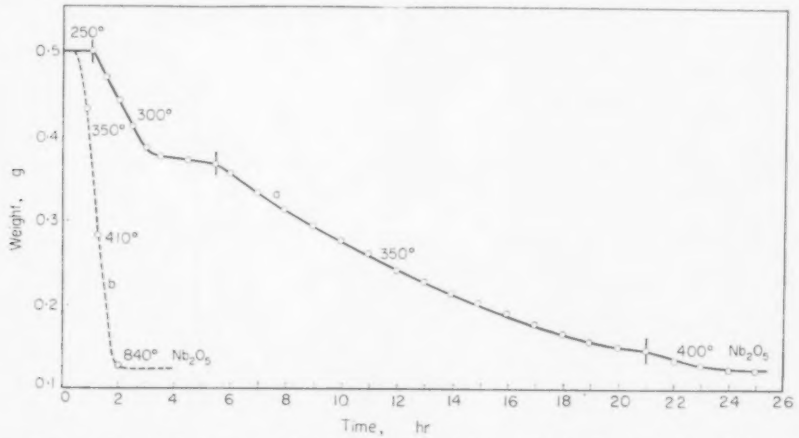

FIG. 1.—Thermolysis curves of niobium oxinate, taken with the Stanton thermobalance at two different rates of heating.

1. The thermolysis curve (Fig. 1) proved the stability of the compound up to 250°. After constant heating, to 400°, decomposition was complete in 24 hr. On increasing the rate of heating, the last traces of oxine sublimed at approximately 600°. The thermolysis curves were taken with a Stanton thermobalance.

2. The absorption spectrum of the emulsion of niobium oxinate in liquid paraffin measured with a Perkin-Elmer, Model 21 infrared spectrophotometer, using a sodium chloride prism, shows a maximum at 10·9 μ which is characteristic of the NbO group[8,9], and which seems to confirm the formula $NbO(C_9H_6ON)_3$. Infrared spectra of niobium oxide and oxine are presented for comparison (Fig. 2).

3. In Fig. 3 the absorption spectrum of niobium oxinate in the ultraviolet-visible region, taken with a grating spectrophotometer (Optica Milano, Model CF_4), is compared with that of oxine. The samples were dissolved in chloroform at a molar concentration of 1×10^4 and the absorption was measured against the solvent.

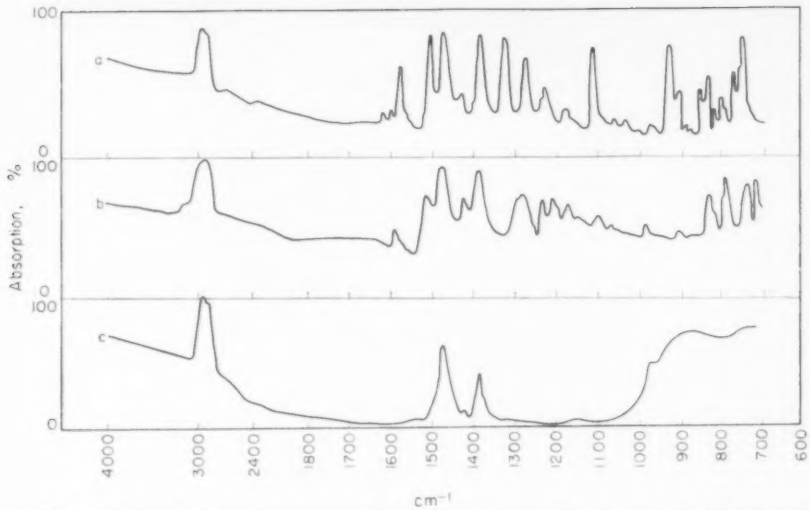

FIG. 2.—Infrared absorption spectra of (*a*) niobium oxinate, (*b*) oxine and (*c*) niobium oxide, measured with the Perkin-Elmer, Model 21, spectrophotometer

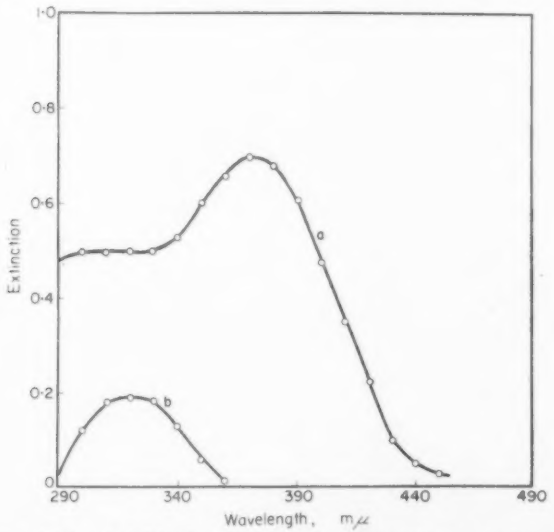

FIG. 3.—Ultraviolet and visible absorption spectra of (*a*) niobium oxinate and (*b*) oxine, taken with the grating spectrophotometer CF4, Optica, Milano

4. Figs. 4 and 5 represent the photomicrographic (Reichert MeF optical microscope) and electron microscopic pictures (AEG-Zeiss, EM 8) of the precipitate and these disclose, together with the electron diffraction picture (Fig. 6), the crystalline nature of niobium oxinate when prepared by the procedure described.

5. Since data on the solubility of niobium oxinate are lacking, some determinations were made by the radiometric and the classical method in the solvents listed in Table II. The measurements were made by shaking samples in a thermostatted room (24°) for 24 hr with the selected solvent. The results in Table II represent the mean value of

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FIG. 4.—Photomicrographs of the crystals of niobium oxinate

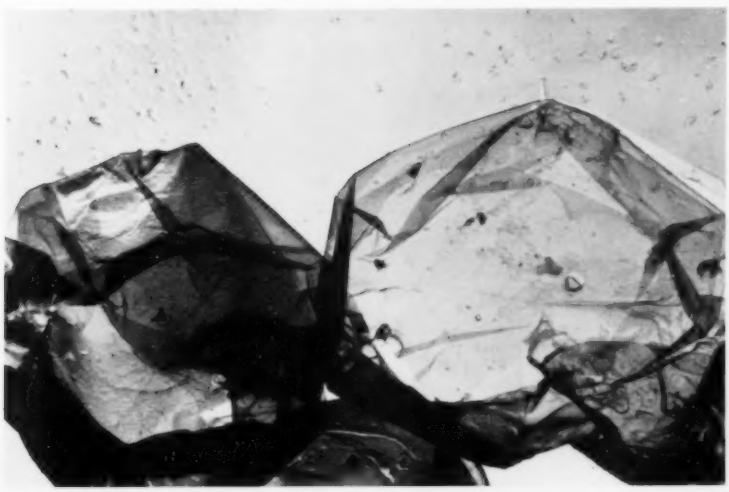

FIG. 5.—Electron-microscopic picture of crystallised niobium oxinate
(Electron microscope AEG–Zeiss, EM8)

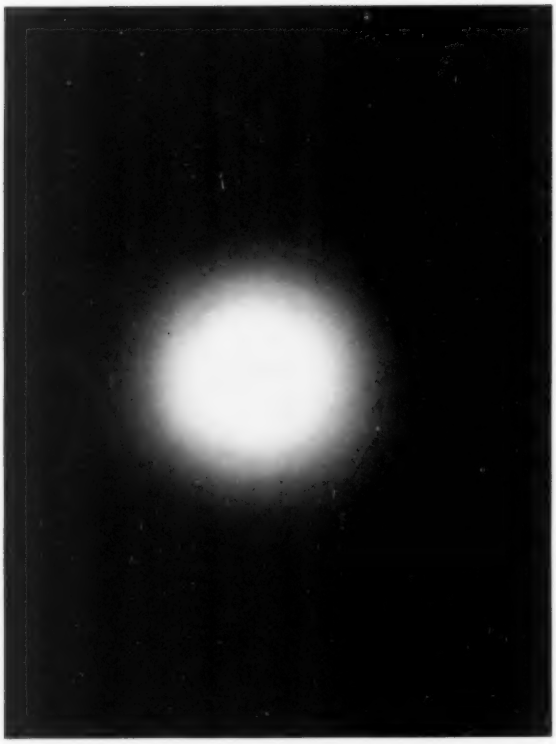

FIG. 6.—Electron-diffraction picture of niobium oxinate.

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TABLE II.

Solvent	Solubility, *mg/ml*
Chloroform	11·2
Acetone	0·65
Ethyl alcohol	0·62
Diethyl ether	0·01
Tetrahydrofuran	1·4
Isopropyl alcohol	0·22
Methyl isobutyl ketone	0·15

6–8 determinations, but there is considerable inconsistency between individual measurements.

Tentative measurements were also made with amyl acetate, nitromethane, mesityl oxide, nitrobenzene, carbon tetrachloride, methyl isopropyl ketone, cyclohexanone, carbon bisulphide and toluene. Of these only nitrobenzene and nitromethane readily dissolved niobium oxinate (6·6 and 1·3 mg/ml, respectively), and other solvents dissolved less than 0·5 mg/ml of the compound.

Like other oxinates, niobium oxinate fluoresces intensely in ultraviolet light.

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Zusammenfassung—Da es den Anschein hat, dass die Zusammensetzung des Nioboxinates, wenn aus wässriger Lösung gefällt, nicht wohldefiniert ist, wurden verschiedene Methoden angewandt um einen stöchiometrisch zusammengesetzten Niederschlag zu erhalten. Von allen studierten Methoden liefert die Fällung von Nioboxinat aus homogener Lösung durch Hydrolyse von Harnstoff die besten Resultate. Die Kristalle sind gut entwickelt und die Zusammensetzung des Niederschlages entspricht innerhalb eines halben Prozentes der Formel $NbO(Oxin)_3$. Die Löslichkeit des Niederschlages in verschiedenen organischen Solventien, die UV- und IR-Spektren sowie Elektronenbeugung wurden untersucht; Thermolysiskurven und Mikrophotographien wurden gemacht.

Résumé—Comme la composition de l'oxinate de niobium, précipité en solution aqueuse, ne semble pas être définitivement établie, de nombreuses techniques nouvelles sont utilisées pour la préparation d'un composé bien défini. Parmi les méthodes étudiées, la précipitation en milieu homogène d'oxinate de niobium par l'urée conduisait aux meilleurs résultats. Le produit est cristallin et correspond à la composition $NbO(C_9H_6ON)_3$, à $\pm$ 0,5 pour cent près. Les solubilités dans différents solvants organiques ont été étudiées, ainsi que les spectres ultraviolet et infrarouge et la diffraction électronique la thermolyse a été effectuée, et des micrographies des cristaux ont ètè prises.

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PRELIMINARY COMMUNICATIONS

Contributions to the basic problems of complexometry—V
Mutual masking of iron and manganese

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THE masking of iron with triethanolamine[1] in the complexometric determination of calcium, magnesium or manganese is widely used in the analysis of lime, dolomite and other calcareous materials such as cements, glasses, *etc*. Using a modified procedure[2] it is possible to mask relatively large concentrations of iron as the colourless complex with triethanolamine. The determination of manganese in the presence of iron in an alkaline reducing medium (hydroxylamine) can be carried out without difficulty, and this fact has been utilised with success in the analysis of ferromanganese.[3] This method has recently been re-examined and modified slightly.[4,5]

More difficulties occur in the screening of manganese. Only small amounts of this element can be masked by triethanolamine because of the formation of an intensely green Mn^{III}-TEA complex.[6] Only recently, a relatively simple method has been developed that enables the masking of manganese in amounts up to 80 mg.[7] The method is based on the fact that in a strongly alkaline medium containing triethanolamine, the manganese is oxidised by atmospheric oxygen to a deep green Mn^{III}-TEA complex. On adding potassium cyanide and raising the pH to 10 with acetic acid, a colourless or slightly yellow $Mn(CN)_4^{3-}$ complex is formed. This method can be used for determination of calcium, or of the sum of calcium and manganese, provided that iron and aluminium have first been separated by precipitation with pyridine.

As triethanolamine itself is a very good masking agent for iron as well as for aluminium, it was thought that it might be possible to find a procedure that would work without first precipitating iron and aluminium. This would be especially useful for various materials rich in manganese, such as manganese slags, welding fluxes, *etc*.

Preliminary experiments were aimed at a transformation of both the iron and the manganese into the Fe-TEA and $Mn(CN)_6^{3-}$ complexes, because only these complexes ensure the complete screening of both elements in complexometric titrations. To the solutions of manganese and iron were added triethanolamine, potassium cyanide, and ammonia or sodium hydroxide, under various conditions, and over various ranges. In view of the alkaline reaction of all the reagents added, the possibility of preventing the precipitation of ferric or manganic hydroxides was carefully studied; such precipitation would make subsequent complexometric titrations impossible. The following procedure proved to be satisfactory.

Procedure

To an acid solution of iron and manganese add excess of 20% triethanolamine in such a way as to avoid the precipitation of hydroxides. Then add at once 20–30 ml of concentrated ammonia containing 1–2 g potassium cyanide. The solution becomes orange and on heating changes to colourless or slightly yellow. Ferric ions form ferricyanide, which immediately oxidises manganese according to the equation:

$$Fe(CN)_6^{3-} + Mn(CN)_6^{4-} = Fe(CN)_6^{4-} + Mn(CN)_6^{3-} \quad (1)$$

The resulting solution contains both complex cyanides of $iron^{II}$ and $manganese^{III}$, which are complexometrically inactive. The reaction proceeds quantitatively, if the solution contains more iron than is equivalent to the manganese according to equation (1). If the solution contains more manganese than iron, part of the manganese remains unoxidised as $Mn(CN)_6^{4-}$ and can be titrated with EDTA (see Table 1, experiments 6–9). With iron deficiency there is no quantitative relation between iron and manganese concentrations, because manganese is partly oxidised by atmospheric oxygen. Excess of iron does not interfere in the titration because ferrocyanide is first formed according to equation

(1) and the excess is then bound as the stable Fe-TEA complex. The presence of large amounts of free ferricyanide is improbable, the solutions being almost colourless.

A series of experiments was carried out in manner described. In some of them the consumption of EDTA was determined (blank experiments—see Table I, experiments 10–12), in others the taken EDTA used was determined by back-titration with calcium chloride, after proper masking. With iron and manganese properly screened, the losses of EDTA were within experimental error, that is 0·02 ml.

TABLE. I.—MUTUAL MASKING WITH VARYING Fe:Mn RATIO. AFTER Fe AND Mn WERE MASKED EDTA WAS ADDED AND TITRATED WITH $CaCl_2$.

No.	*ml*			*ml*		0·05*M* EDTA *ml*
	Fe	Al	Mn	Taken	Found	
1	4·94	—	0·51	2·01	2·00	−0·01
2	5·14	—	5·10	2·01	1·99	−0·02
3	4·94	1·05	3·06	2·01	2·00	−0·01
4	11·65	25·96	2·98	19·86	19·79	−0·07
5	23·30	20·76	9·95	9·93	9·90	−0·03
6	2·96	—	5·10	2·01	1·29	−0·72
7	4·45	—	5·10	2·01	1·14	−0·87
8	4·94	—	5·10	2·01	0·80	−1·21
9	2·96	10·47	5·10	5·03	2·81	−2·22
10	10·79	—	9·46	0·07[a]		
11	21·58	—	18·91	0·09[a]		
12	21·58	—	18·91	0·11[a]		

[a] Consumption of EDTA by direct titration.

During further experiments some unexpected difficulties occurred in the complexometric determination of alkaline earths because of the formation of a white crystalline precipitate in the solutions of complex Fe- and Mn-cyanides. The cause of it is formation of calcium salts of manganese^{III} cyanide, which dissolves with difficulty in EDTA even in hot solution.

CONCLUSIONS

It can be presumed that by this simple procedure the selectivity of the complexometric determination of calcium or magnesium may be improved for the following reasons:

(1) The determination is not affected by iron, aluminium or manganese.

(2) The addition of potassium cyanide also masks other elements (Ag, Hg, Zn, Cd, Ni, Co, Cu).

(3) Other heavy elements, such as lead or bismuth, if present, can be masked by other complex-forming reagents such as BAL[8] or thioglycollic acid.[9]

Summary—The screening of iron and manganese in some further complexometric titrations has been studied. It was found that by masking with triethanolamine and potassium cyanide, ferricyanide is formed, which immediately oxidises manganese according to the equation:

$$Fe(CN)_6^{3-} + Mn(CN)_6^{4-} = Mn(CN)_6^{3-} + Fe(CN_6)^{4-}$$

The resulting solutions contain both the complex cyanides of iron(II) and manganese(III), which are "complexometrically" inactive. The difficulties in further determinations after proper masking of iron and manganese are mentioned.

Zusammenfassung—Die Maskierung von Eisen und Mangan in einigen weiteren chelometrischen Titrationen wurde studiert. Beim Maskieren mit Triäthanolamin und Kaliumcyanid wird das Eisen in Ferricyanid übergeführt, welches das Mangan sofort nach folgender Gleichung oxydiert

$$Fe(CN)_6^{3-} + Mn(CN)_6^{4-} \rightleftharpoons Mn(CN)_6^{3-} + Fe(CN)_6^{4-}$$

Die resultierende Lösung enthält die komplexen Cyanide von Eisen(II) und Mangan(III), welche

"komplexometrisch" inaktiv sind. Schwierigkeiten werden diskutiert, die bestehen, wenn in der Lösung andere Metalle bestimmt werden sollen.

Résumé—Les auteurs ont étudié le comportement du fer et du manganese dans quelques titrages complexométriques. En complexant avec de la tritéhanolamine et du cyanure de potassium, il se forme du ferricyanure qui oxyde immédiatement le manganèse suivant la réaction:

$$Fe(CN)_6^{3-} + Mn(CN)_6^{4-} \rightleftarrows Mn(CN)_6^{3-} + Fe(CN)_6^{4-}$$

Les solutions résultantes contiennent les complexes cyanure du fer(II) et du manganèse(III), qui sont inactifs "au point de vue complexométrie". Les difficultés rencontrées dans les déterminations ultérieures, après que le fer et le manganèse aient été complexés, sont mentionnées.

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Extraction of As^V from H_2SO_4–KBr solutions and its analytical use

(*Received* 16 *January* 1961)

It has long been known that some halides of As^{III} and As^V may be extracted into organic solvents. Thus, the extraction of As^{III} from HCl medium into tetrachloromethane,[1,2] ether,[3] dichlorodiethylether,[4] and other solvents,[5] has been described; so also has the extraction of As^V from the same medium into ether,[6] tetrachloromethane,[6] and isobutylmethylketone.[7]

The extraction of other halides of arsenic has not been studied so closely. Bock and co-workers[8] describe the extraction of $AsBr_3$ into ether and Brinck and co-workers[5] describe the extraction of As^{III} from HI solution. None of the methods mentioned is quantitative.

It is known that some relation exists between extraction and distillation of certain covalent compounds. In the literature the distillation of As^V from H_2SO_4-KBr medium[9] has been described and has been successfully applied. For this reason the extraction of As^V from this medium into organic solvents was investigated.

This extraction is found to be easily reproducible. An optimum concentration of sulphuric acid is 14–17*N*; at lower concentration the extraction is not quantitative, and in 10*N* acid does not take place at all. At higher concentration, HBr and Br_2 are freely liberated, and the phases are difficult to separate.

The necessary amount of KBr is about 200 mg for the extraction of 100 μg of arsenic from 25 ml; with smaller amounts of KBr the extraction does not take place quantitatively, but larger amounts of KBr do not interfere.

Many organic solvents were studied. Preliminary investigations showed tetrachloromethane to be the best. Alcohols, ketones and ethers are unsuitable because of their high solubility in the aqueous medium.

When 100 μg of arsenic were extracted from the H_2SO_4-KBr medium described into 25 ml of

tetrachloromethane, and the arsenic was then re-extracted with 25 ml of water and neutralised with sodium hydroxide, photometric determination through molybdenum blue showed that the extraction and re-extraction of arsenic are very rapid and quantitative. From the character of the reaction a high selectivity is to be expected, and this selectivity has been proved experimentally.

The extraction of arsenic by this procedure will be more fully described in a further communication.

Acknowledgement—It is my pleasant duty to thank Dr. R. Přibil for his interest in this work.

Summary—By the use of tetrachloromethane, arsenic^{V} can be completely extracted from a 14-17*N* aqueous sulphuric acid solution containing 200 mg of potassium bromide per 25 ml of solution.

Zusammenfassung—Tetrachlorkohlenstoff ist geeignet fünfwertiges Arsen aus Lösungen zu extrahieren, die 14–17 normal in Schwefelsäure sind und etwa 200 mg Kaliumbromid per 25 ml Lösung enthalten.

Résumé—En utilisant le tétrachlorométhane, l'arsenic (V) peut être extrait à partir d'une solution aqueuse d'acide sulfurique 14–17 *N* contenant environ 200 mg de bromure de potassium pour 25 ml. de solution.

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Applications de la chelatometrie—VII. Dosage volumetrique des *ortho*-acyl-phenols

(*Received* 15 *December* 1960)

INTRODUCTION

Les ortho-acyl-phénols trouvent actuellement un débouché industriel croissant, notamment pour la fabrication des γ-benzopyrones (chromones, flavones et isoflavones) et des coumarines substituées.

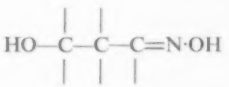
Ils sont généralement préparés par réaction de Fries[1] à partir des esters phénoliques correspondants et on sait que cette réaction conduit toujours, bien que dans des proportions variables, aux deux isomères ortho et para en même temps qu'une décomposition partielle régénère le phénol de départ.

Le dosage de l'isomère ortho en présence de l'isomère para et de phénols non acylés n'a guère été étudié à notre connaissance: Fritz et Keen ont montré la possibilité de doser les phénols substitués de cette famille par anhydrotitrimétrie dans la diméthyl-formamide comme solvant et en présence d'azo-violet comme indicateur[2]; toutefois cette méthode ne permet pas de distinguer les constituants du mélange signalé ci-dessus qui sont dosés tous ensemble; de Lorenzi et Credali ont appliqué une méthode identique dans le cas particulier de la para-hydroxypropiophénone[4] tandis que Baudet et Pacheco opéraient en milieu alcoolique[12] avec l'aide du bleu C-4-B et que Mouton et Masson

décrivaient un procédé spectrophotometriqué dans l'U.-V. pour le même produit[3]; nous n'avons pas expérimenté cette dernière technique sur les mélanges précités, désireux que nous étions de trouver une méthode générale pour tous les acyls-phénols en position ortho. Ramanujam a récemment publié un mode de dosage par bromométrie des corps de la série des hydroxyacétophénones,[4] mais cette technique ne résoud pas non plus le problème que nous préoccupe.

PRINCIPE

Le procédé dont nous avons eu l'idée repose sur une observation d'Ephraim[5] qui dés 1931 remarqua que le groupe



était spécifique du cuivre avec les ions duquel il donnait des précipités quantitatifs à la manière de l'aldéhyde salicylique dont l'emploi pour le dosage gravimétrique du cuivre et du nickel est bien connu. D'autres auteurs ont appliqué ensuite les oximes de différents corps de cette série également pour le dosage du nickel[6-8] du palladium[7], du vanadium[7,10], du zinc[9], du cobalt[8] et du titane[7]. Il semble bien toutefois, d'après nos essais, que le cuivre est le métal le plus généralement précipité par les oximes de ce groupe et nous avons finalement retenu celuici pour la mise en oeuvre de note procédé: aprés oximation de l'échantillon par un moyen classique tel que l'emploi du chlorhydrate d'hydroxylamine en milieu alcalin, la solution résultante est traitée par une liqueur contenant un sel de cuivre en quantité connue et ayant un effet tampon convenable sur le pH du milieu réactionnel. Aprés filtration on titre le cuivre restant dans le filtrat et détermine la quantité d'ortho-acyl-phénol par différence.

Aprés divers essais, nous avons retenu une méthode chélatométrique avec indicateur métallochrome comme étant la plus intéressante pour évaluer volumétriquement le cuivre dans le filtrat. Nous avons parallélement controlé la possibilité de doser le cuivre présent dans le précipité.

Nous poursuivons actuellement nos travaux sur un certain nombre d'acyl-phénols variés.

Les résultats de ces travaux seront publiés ultérieurement dans cette revue avec le détail du mode opératoire.

Augers-en-Brie,
(S et M.), France

CLAUDE HENNART®
avec la collaboration de
(*Mme.*) YVETTE LEFEVRE
pour la partie expérimentale

Résumé—Les ortho-Acyl-Phénols, tels que l'ortho-hydroxyacetophénone et ses homologues, peuvent être dosés volumétriquement après oximation. On précipite le complexe cuivrique et un dosage chélatométrique est effectué.

Summary—The ortho-acyl-phénols, such as ortho-hydroxyacetophenone and its homologues, can be determined titrimetrically after oximation. The precipitation of cupric complex is carried out and subsequent titration is made by chelatometry.

Zusammenfassung—Die ortho-Acyl-Phenollen, ist wie die ortho-oxyacetophenon und ihre Homologe, können volumetrisch bestimmt werden nach Oximation. Die Kupferzusammensetzung wird gefällt und chelatometrisch bestimmt.

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LETTER TO THE EDITOR

Explosion in analytical laboratory of Jas. Anderson & Co. (Colours) Ltd. on Friday 13th January, 1961

SIR:

WHILE carrying out a wet oxidation of a red azo pigment, C.I. Pigment Red 38, using the method of G. Frederick Smith and Harvey Diehl from *Talanta*, 1960, **4**, 185, a violent explosion occurred. The authors described the reaction as "hazard free" but this is clearly not the case.

The wet oxidation technique was being considered for use in the trace metals analysis of pigments and a sample was being examined as follows using a slight modification of the Bethge apparatus.

Five g of sample were added to the 250-ml round bottomed flask with 15.0 ml of 60% perchloric acid, 3.0 g of 50/50 W/W paraperiodic acid and 1 mg of sodium metavanadate. No reaction took place immediately and slight heat was applied to agitate the mixture and promote the reaction. After 2–3 min heat was removed and the reaction proceeded as suggested, with iodine being liberated and subliming into the reflux apparatus and eventually into the condenser. The reaction slowed down considerably but by this time the pigment had been wetted out, although the bulk of it was still unaffected. Slight heat was again applied, and reaction slowly advanced until a boiling action commenced, but at this time only 2–3 ml of liquid had refluxed, and was now lying in the trap of the return apparatus. (This was possibly water owing to the low temperature.)

Suddenly the mixture in the flask began to darken considerably until it was black and one or two small flames appeared for an instant. Heat was removed, the safety shield put in place, the fume cupboard window closed and a safe position adopted. The flashes had by this time increased in number and proportions, and every 5 sec or so a more violent flash would bump the entire apparatus and leap up the tube to the exit of the condenser. After about a minute from the time of darkening, the flask completely shattered with an explosion which splashed the acid and glass fragments around the inside of the fume cupboard but left the reflux system and condenser intact.

Owing to the warning signs and time lag of the explosion no injuries were sustained by the operator.

Hawkhead Road
Paisley, Scotland
16 *January* 1961

J. THOMSON

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NOTICES

The following meetings have been arranged in the Bourquelot lecture theatre, Faculty of Pharmacy, Paris, at 5.45 p.m., under the direction of Professors J. A. GAUTIER and P. MALANGEAU:

Tuesday 11 *April* 1961: *Lithium Aluminium Hydride as a Reagent in Analytical Chemistry:* M. E. A. M. DAHMEN.

Tuesday 25 *April* 1961: *Ionisation Constants and Structures of Organic Compounds:* Professor P. RUMPF.

Tuesday 9 *May* 1961: *Determination of Gases and Toxic Vapours by Galvanic Piles (Osmopiles):* M. A. BERTON.

Tuesday 30 *May* 1961: *Humidity and Dry Extract of Foodstuff Materials and Drugs:* Pharmacien Lieutenant-Colonel J. KIGER.

The following meetings have been arranged:

Wednesday 3 *May* 1961: **Society for Analytical Chemistry:** Meeting for reading of Original Papers. Burlington House, London, W.I. 7.00 p.m.

Friday 12 *May* 1961: **Society for Analytical Chemistry,** Midlands Section and Microchemistry Group: Joint Meeting: *Automation in the Analytical Laboratory.* Technical College, Nottingham. 7.15 p.m.

Friday–Saturday 26–27 *May* 1961: **Society for Analytical Chemistry,** Midlands Section and Western Section: Joint Meeting. Hereford. *Friday:* Afternoon visit to Bulmers (Cider) Ltd.

Evening lecture on *Use of Ion-Exchange and Column Chromatography in Metallurgical Analysis.* Town Hall, Hereford.

Saturday: Morning coach tour of countryside around Hereford. Evening dinner at *Green Dragon Hotel*, Hereford.

Sunday-Friday 16–21 *July* 1961: Symposium on *The Teaching of Analytical Chemistry.* University of Aberdeen, Scotland.

The symposium will take the form of a series of discussions on the teaching of analytical chemistry, considered first in its own right, then in conjunction with the other branches of chemistry. A social programme and a ladies' programme have been arranged.

Monday 17 *July*

9.30 a.m. Opening of Symposium: Professor G. M. BURNETT.
The Teaching of Analytical Chemistry:
(*a*) *Theory:* Dr. R. A. CHALMERS.
2.30 p.m. (*b*) *Practical Work:* Mr. L. S. BARK and Mr. L. DAVIES.

Tuesday 18 *July*

9.30 a.m. *Analytical and Organic Chemistry:* Professor S. VOEIBEL.

Wednesday 19 *July*

9.30 a.m. *Analytical and Inorganic Chemistry:* Dr. G. W. A. FOWLES.
2.30 p.m. *Analytical and Physical Chemistry:* Professor F. ČŮTA.

Friday 21 *July*

9.30 a.m. *The Teaching of Chemistry in Czechoslovakia:* Dr. J. ZÝKA.

Further details may be obtained from Miss D. A. THOMSON, Chemistry Department, The University, Old Aberdeen, Scotland.

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Sunday–Friday 13–18 *August* 1961: **Metropolitan Microchemical Society** under the sponsorship of the **International Union of Pure and Applied Chemistry:** *International Symposium on Microchemical Techniques*. Pennsylvania State University, U.S.A.

The technical programme will consist of a number of main introductory lectures and a full schedule of invited papers directed toward new methods and techniques or unique applications of microchemical or microanalytical interest.

A series of social activities will be held to facilitate the informal meeting of the participants. In addition, a ladies' programme is planned.

A commercial exhibit of laboratory equipment, chemicals and specialities will be held in conjunction with the meeting programme. It is also hoped to schedule one session at which participants can demonstrate novel, non-commercialised techniques and apparatus which they have personally developed.

Further details may be obtained from Mr. HOWARD J. FRANCIS, Jr., c/o Pennsalt Chemicals Corporation, Post Office Box 4388, Philadelphia, Pennsylvania, U.S.A.

Monday–Wednesday 18–20 September 1961: **Canadian Association for Applied Spectroscopy:** *Eighth Ottawa Symposium on Applied Spectroscopy*. Ottawa.

Papers are invited for presentation on the subjects of applied spectroscopy, including emission, ultraviolet, infrared, X-ray and nuclear magnetic resonance work in the field of instrumental analysis.

Titles and brief abstracts of papers should be submitted before 6 June, 1961, to ROLAND LAUZON, Programme Chairman, Eighth Ottawa Symposium on Applied Spectroscopy, c/o Division of Pure Chemistry, National Research Council, Ottawa, Ontario, Canada.

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B.S.I. News announces the following addendum to a British Standard:

Addendum I: 1960 *to B.S.* 2690: *Methods of testing water used in industry*. It provides methods for determining solids content, carbon dioxide, dissolved silica, total iron and dissolved oxygen in high purity water. (Price 6s.)

The following revised British Standard is also announced:

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 10: 1960: *Arsenic in coal and coke*. A colorimetric method, using either wet or dry oxidation, and a paper stain (modified Gutzeit) method for arsenic are described. (Price 6s.)

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PAPERS RECEIVED

The distribution of vanadium between alcoholic hydrochloric acid solutions and the strongly basic anion-exchanger Dowex-1: Separation of vanadium and nickel from iron and copper. G. E. JANAUER and J. KORKISCH. (28 *January* 1961).

Über die Anwendung von Cystein als Maskierungsreagens bei komplexometrischen Titrationen. WOLFGANG BERNDT und JOSEF ŠAŔA. (28 *January* 1961).

Contributions to the basic problems of complexometry—VI: The masking of tervalent chromium. RUDOLF PŘIBIL and VLADIMIR VESELÝ. (30 *January* 1961).

Diammonium-5,5′-indigeo disulphonate as an analytical reagent—I: Gravimetric determination of thorium and cerium^{III} and their separation from uranium^{VI}. B. D. JAIN and J. J. SINGH. (6 *February* 1961).

Applications of infrared spectroscopy—V: The retention of water and organic solvents by carbohydrate materials. D. M. W. ANDERSON and N. J. KING. (6 *February* 1961).

Sur un principe de colorimétrie en milieu non-aqueux—II: Emploi du bromure de p-nitrophènacyle pour l'identification et le dosage des acides carboxyliques. JAROSLAV BARTOS. (6 *February* 1961).

Iodemetric determination of copper and iron in one solution. J. AGTERDENBOS and E. J. v. TELLINGEN. (8 *February* 1961).

Gravimetric determination of tungsten by homogeneous precipitation. R. DAMS and J. HOSTE. (9 *February* 1961).

Eine neue Methode zur spektrophotometrischen Bestimmung von Mikrogrammengen Titan. J. KORKISCH. (14 *February* 1961).

Determination of ferrocyanides. G. V. L. N. MURTHY and T. S. VISWANATHAN. (18 *February* 1961).

Die Bestimmung kleiner Fluormengen—I: Eine kritische Übersicht. ROMAN VALACH. (20 *February* 1961).

EDTA as a complexing reagent in strip paper chromatographic separation of some metal ions. ERIC JOHN SINGH and ARUN K. DEY. (21 *February* 1961).

The determination of traces of palladium in samples of platinum by neutron-activation analysis. R. A. KILLICK and D. F. C. MORRIS. (22 *February* 1961).

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Applicaciones analiticas del AEDT y analoges: F. BERMEJO and A. PRIETO. Imprenta del Seminario Conciliar, Santiago de Compostela, 1960. Pp. xii + 625. $10.00.

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Proceedings of the Symposium on the Chemistry of Co-ordination Compounds, Agra, February 7 and 8, 1959: In three parts. National Academy of Sciences, India, Lajpatrai Road, Allahabad, India, 1960. Part I, pp. iii + 148. Rs. 15.00. Part II, pp. ii + 203. Rs. 25.00. Part III, pp. x + 302. Rs. 35.00. Three parts, Rs. 75.00.

The Radiochemistry of Beryllium: A. W. FAIRHALL. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., May, 1960. NAS-NS 3013 Pp. v + 58. $0.75.

The Radiochemistry of Indium: D. N. SUNDERMAN and C. W. TOWNLEY. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., May, 1960. NAS-NS 3014 Pp. vi + 46. $0.50.

The Radiochemistry of Zinc: HARRY G. HICKS. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., June 1960. NAS-NS 3015. Pp. vi + 58. $0.75.

The Radiochemistry of Protactinium: H. W. KIRBY. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., December 1959. NAS-NS 3016. Pp. vi + 80. $1.00.

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VERFAHREN ZUR BESTIMMUNG GERINGER MENGEN, DAS JOD IN VERSCHIEDENEN OXYDATIONS-ZUSTÄNDEN ENTHALTENDER JODVERBINDUNGEN NEBENEINANDER

E. SCHULEK und L. BARCZA
Institut für anorganische und analytische Chemie der L. Eötvös Universität, Budapest

(*Received* 23 *May* 1960: *Accepted* 6 *January* 1961)

Zusammenfassung—Ein aus Jodid, Jod, Hypojodit, Jodat und Perjodat bestehendes System ist labil und kann nur bei höheren pH-Werten und nur vorübergehend existieren. Verfasser reduzierten das Perjodat nach Zersetzung des Hypojodits mittels Phenol mit Hilfe einer überschüssigen Menge arseniger Säure und titrierten deren Überschuss zurück. Das Jodat wurde nach Reduktion des Jods und Hypojodits mittels Phenol jodometrisch bestimmt. In Gegenwart von Perjodat muss die dem Perjodat äquivalente, durch die Arsenit-Reduktion des Perjodats gebildete Menge Jodat in Abzug gebracht werden. Die gesamte Menge Hypojodit und Jod wurde aus der Differenz der jodometrischen Messungen (mit und ohne Phenol) berechnet. Nach Bestimmung der Gesamtmenge der oxydierenden Stoffe kann die Gesamtmenge Jodid in Gegenwart von p-Äthoxychrysoidin als Adsorptionsindikator mit Silbernitrat gemessen werden. In Abwesenheit von Perjodat wurde das elementare Jod neben Hypojodit unter Ausnutzung jenes Prinzips bestimmt, wonach das Thiosulfat durch Hypojodit zu Sulfat, durch Jod aber zu Tetrathionat oxydiert wird. Letzteres konnte nach dem Verfahren von Kurtenacker und Fritsch ermittelt werden. Die Ergebnisse sind zufriedenstellend.

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JODVERBINDUNGEN, die das Jod in verschiedenen Oxydationszuständen enthalten, können im allgemeinen nur in einem bestimmten pH-Bereich nebeneinander existieren.

Elementares Jod, Jodid und Hypojodit können nebeneinander etwa zwischen pH = 7 und 13 bestehen, bei niedrigeren pH-Werten verschiebt sich das zwischen den Komponenten bestehende Gleichgewicht:

$$J_3^- + OH^- \rightleftharpoons JOH + 2J^- \quad (1)$$

vollkommen in Richtung des Jods, bei höheren pH-Werten in Richtung des Hypojodits. Obige Gleichung lässt auch den Einfluss der Jodid–Konzentration erkennen. Hinsichtlich der Klärung der kinetischen Verhältnisse dieser Reaktion sind die Untersuchungen Skrabals[1] von grundlegender Wichtigkeit. Die Frage wird durch die rasche Disproportionierung des Hypojodits zu Jodat noch weiter erschwert:

$$3JO^- = JO_3^- + 2J^- \quad (2)$$

Jodat und Jodid können über pH = 8 auch längere Zeit hindurch nebeneinander existieren, bei einem niedrigeren pH-Wert spielt sich jedoch die allgemein bekannte—auch zur Messung der Wasserstoffionen verwendbare—Reaktion

$$JO_3^- + 5J^- + 6H^+ = 3J_2 + 3H_2O \quad (3)$$

bereits ab.

Die Reaktion zwischen Perjodat und Jodid[2] läuft unter Bildung von Jodat und Jod (bzw. in Abhängigkeit vom pH-Wert auch Hypojodit) bei pH = 8 bereits ab,

$$JO_4^- + 2J^- + H_2O = JO_3^- + J_2 + 2OH^- \quad (4)$$

wird jedoch bei höheren pH-Werten derart langsam, dass die beiden Ionen (JO_4^- und J^-) vorübergehend auch nebeneinander bestehen können.

Beim Ansäuern wird das Perjodat vollkommen reduziert:

$$JO_4^- + 7J^- + 8H^+ = 4J_2 + 4H_2O \qquad (5)$$

Auch die obigen Reaktionsgleichungen lassen erkennen, dass bei dauernd hohem pH-Wert nur das Jodat–Jodid System existiert, alle anderen Komponenten gehen in dieses über, bei niedrigem pH-Wert hingegen führen die Prozesse zur Bildung von Jod (bzw. dem Jodid–Komplex des Jods).

Die analytische Untersuchung dieser miteinander in verwickelten Gleichgewichten stehenden Systeme ist—besonders bei niedrigen Konzentrationen—eine schwere und bisher noch ungelöste Aufgabe.

Lonnes[3] schlägt zur Bestimmung von Jod, Hypojodit und Jodat nebeneinander die kolorimetrische Ermittlung des Jods, Titration des Hypojodits und Jods mit Arsenit in der ursprünglichen (alkalischen) Lösung und nach Ansäuern Titration des aus dem Jodat ausgeschiedenen Jods mit Thiosulfat vor. Mit dieser Frage beschäftigte sich auch Péchard.[4] Sammet[5] bestimmt die Summe des Jods und Hypojodits sowie das Jodat nach ähnlichen Prinzipien, bestimmt das Jod bzw. das Hypojodit jedoch nicht getrennt. Demgegenüber ermittelt er das gesamte Jod (inbegriffen auch das Jodid) in Form von elementarem Jod in einem neuen Anteil der Lösung nach einer auf eine Reduktion drauffolgenden milden Oxydation. Der so freigemachte Gesamtjod wird nun mit Tetrachlorkohlenstoff ausgeschüttelt und gemessen. Mit der Bestimmung von Perjodat, Jodat, Jod und Jodid nebeneinander beschäftigten sich Scharrer und Schwaibold.[6]*

Wir beschäftigten uns zuerst mit der Bestimmung von relativ viel Jodid, elementarem Jod und Hypojodit nebeneinander d.h. also mit der Bestimmung des Jods mit den Oxydationszahlen -1, 0 *und* $+1$. Da zwischen diesen Formen ein Gleichgewicht besteht, musste ein Reagenz gefunden werden, das sowohl mit elementarem Jod, als auch mit Hypojodit, jedoch mit beiden auf andere Art reagiert. Diesem Zweck entspricht das Phenol nicht (obzwar es die Bestimmung von Jodat in Gegenwart von Jod bzw. Hypojodit ermöglicht[7]), da das im Überschuss angewandte Phenol das Gleichgewicht zwischen dem elementaren Jod und Hypojodit verschiebt. Kolthoff empfiehlt dieses Verfahren in der deutschen Ausgabe seines bekannten Handbuches[8] nach der Besprechung der erwähnten Methode[7] zur Analyse der Preglschen Lösung (ein Jodat, Jod und Hypojodit enthaltendes Gemisch, wahrscheinlich borathaltige alkalische Lösung des Jods) ohne nähere Bezeichnung.

Zur Lösung der Aufgabe ist das Thiosulfat geeignet, das durch Jod mit annähernd der gleichen Geschwindigkeit zu Tetrathionat und durch Hypojodit zu Sulfat oxydiert wird:[9]

$$2S_2O_3^{2-} + J_2 = S_4O_6^{2-} + 2J^- \qquad (6)$$

$$S_2O_3^{2-} + 4JO^- + H_2O = 2SO_4^{2-} + 4J^- + 2H^+ \qquad (7)$$

Hierzu möchten wir erwähnen, dass die direkte Titration mit Thiosulfat—insbesondere im 0,01 n Massstabe—nach unseren Erfahrungen nicht zum Erfolg führt, obzwar einige Autoren dieses Verfahren empfehlen.[4]

Die Ursache hierfür liegt nach den Ergebnissen unserer Untersuchungen einesteils in der Unsicherheit der Indikation (pH $\geqq$ 8) und anderenteils darin, dass das bei der

* Die nur im Referat zur Verfügung stehende Beschreibung des Verfahrens ist uns unüberblickbar.

Jod-Thiosulfat Reaktion gebildete Tetrathionat durch Hypojodit—zumindest teilweise—gleichfalls zu Sulfat oxydiert werden kann. Die Ergebnisse sind weiter von der Geschwindigkeit der Titration abhängig. Auch die Konzentration des Hypojodits kann nach unseren Untersuchungen bei relativ niedrigen Jodid-Konzentration in einer Jodhaltigen Lösung bei pH = 8 nicht mehr vernachlässigt werden. Dies liefert die Erklärung dafür, dass das Jod bei pH = 8 im 0,01 n Massstabe mit Thiosulfat nicht mehr direkt titriert werden kann. Liegt die Jodid-Konzentration höher, so kann der Endpunkt nicht mehr oder nur ungenau beobachtet werden. Die Thiosulfatlösung muss also im Überschuss und auf einmal zugegeben werden.* Der Überschuss wird bei pH = 8 auf Stärkelösung als Indikator mit Jodlösung zurücktitriert. Der Tetrathionat-Gehalt der Lösung lässt sich—gemeinsam mit dem bei der Rücktitration des Thiosulfatüberschusses gebildeten Tetrathionat—nach der Methode von Kurtenacker und Fritsch[10] bestimmen. Das Verfahren beruht darauf, dass das Tetrathionat mit Cyanid in neutralem oder schwach alkalischem Medium nach folgender Gleichung reagiert:

$$S_4O_6^{2-} + CN^- + H_2O = S_2O_3^{2-} + SCN^- + 2H^+ + SO_4^{2-} \qquad (8)$$

Das gebildete Thiosulfat kann unter geeigneten Bedingungen mit Jod titriert werden. Der ursprüngliche Jodgehalt der Lösung kann in Kenntnis des Thiosulfatüberschusses bzw. des aus diesem gebildeten Tetrathionats berechnet werden.

Auch die Menge des Hypojodits lässt sich aus dem Unterschied zwischen dem in bekanntem Überschuss angewandten Thiosulfat und den Daten der Tetrathionat-Messung berechnen.

Da jedoch bei obiger Bestimmung das Äquivalentgewicht des Hypojodit-Jods das Vierfache des Atomgewichts des elementaren Jods beträgt (siehe G1.7), verursacht ein eventueller Fehler bei der Titration eine bedeutende Abweichung. Es ist daher zweckmässiger, das beim Ansäuern eines getrennten Teils der Lösung freigewordene und das ursprünglich vorhandene Jod gemeinsam zu bestimmen und das Hypojodit aus der Differenz zu berechnen.

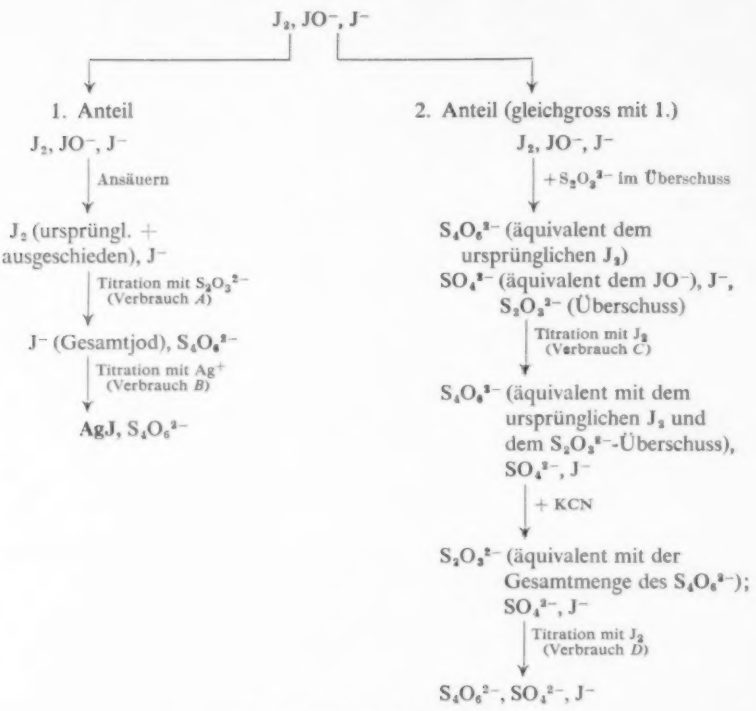
Bei Anwendung dieser Methode kann das ursprünglich vorhandene und das aus der Reduktion des Jods bzw. Hypojodits stammende Jodid in der gleichen Lösung nach entsprechender Verdünnung in Gegenwart von p-Äthoxychrysoidin als Adsorptionsindikator mit Silbernitratlösung direkt titriert werden.[11] Diese Methode wird nämlich durch die Gegenwart des Tetrathionats nicht gestört und so ist es nicht notwendig, einen dritten Anteil langwierig vorzubereiten.—Die zu befolgende Methode ist übrigens im Analysenschema Nr. 1. (siehe dort) kurz zusammengefasst.

Wenn die Lösung ausser relativ viel Jodid, Jod, Hypojodit auch Jodat enthält, d.h. wenn das Jod mit den Oxydationszahlen −I, 0, +I *und* +V *in seinen Verbindungen vorliegt*, so kann das Jodat nach der Titration des freien Jods und des Hypojodits, d.h. nach Rücktitration des Thiosulfatüberschusses bestimmt werden.† Die Lösung wird zu diesem Zweck angesäuert, und das in Freiheit gesetzte Jod mit Thiosulfat titriert.

Man kann auch vorgehen, indem man das bei letzterer Jodat–Jodid–Reaktion

* Bei der Zugabe der Thiosulfatlösung findet eine geringgradige Änderung des pH-Wertes der Lösung statt, diese ist jedoch—da das System in allgemeinen gepuffert untersucht wurde—praktisch vernachlässigbar. Ist die zu untersuchende Lösung nicht gepuffert, muss die Thiosulfatlösung zuerst auf den pH-Wert der untersuchten Lösung eingestellt werden.

† Man darf dabei nicht vergessen, dass die Lösung oder die Thiosulfatlösung auf den pH-Wert der ursprünglichen Lösung gepuffert sein muss.


J_2, JO^-, J^-
1. Anteil
J_2, JO^-, J^-
Ansäuern
J_2 (ursprüngl. + ausgeschieden), J^-
Titration mit $S_2O_3^{2-}$ (Verbrauch *A*)
J^- (Gesamtjod), $S_4O_6^{2-}$
Titration mit Ag^+ (Verbrauch *B*)
AgJ, $S_4O_6^{2-}$
2. Anteil (gleichgross mit 1.)
J_2, JO^-, J^-
+ $S_2O_3^{2-}$ im Überschuss
$S_4O_6^{2-}$ (äquivalent dem ursprünglichen J_2)
SO_4^{2-} (äquivalent dem JO^-), J^-, $S_2O_3^{2-}$ (Überschuss)
Titration mit J_2 (Verbrauch *C*)
$S_4O_6^{2-}$ (äquivalent mit dem ursprünglichen J_2 und dem $S_2O_3^{2-}$-Überschuss), SO_4^{2-}, J^-
+ KCN
$S_2O_3^{2-}$ (äquivalent mit der Gesamtmenge des $S_4O_6^{2-}$); SO_4^{2-}, J^-
Titration mit J_2 (Verbrauch *D*)
$S_4O_6^{2-}$, SO_4^{2-}, J^-

Analyseschema 1

gebildete Jod mit Sulfit bindet und nachher das Tetrathionat bestimmt. In solchen Fällen wird das Jodat in einem separaten Teil der Lösung bestimmt.

Bei dieser Methode hat sich (im Gegensatz zum vorangehenden Fall) Tetrathionat nur in der Reaktion des ursprünglichen Jods und des Thiosulfats sowie bei der Rücktitration des Thiosulfatüberschusses gebildet, da bei der Entfernung des aus dem Jodat gebildeten Jods (siehe G1.3) nur das in dieser Hinsicht indifferente Sulfat entsteht:

$$J_2 + SO_3^{2-} + H_2O = 2J^- + SO_4^{2-} + 2H^+ \qquad (9)$$

In diesem Falle wird das Jodat in einem getrennten Anteil der Lösung bestimmt, wobei durch Alkalischmachen auch das Jod zu Hypojodit umgesetzt und mit Phenol gebunden wird:[7]

$$J_2 + C_6H_5OH + OH^- = JC_6H_4OH + J^- + H_2O \qquad (10)$$

Wir möchten hierzu bemerken, dass das Jodat unter den gegebenen Umständen unverändert bleibt, und nach Ansäuern der Lösung jodometrisch bestimmt werden kann, da das elementare Jod in saurem Medium mit Phenol nicht mehr reagiert. Dieses Verfahren wird noch eingehender besprochen. Vorläufig verweisen wir auf die Analysenschemata 2 und 3.

Ein Jodid, Jod, Hypojodit, Jodat und Perjodat enthaltendes System (Jod mit den Oxydationszahlen −I, 0, +I, +V *und* +VII) *kann nur vorübergehend bestehen.* In diesem System reagiert das Perjodat im Gegensatz zu Jodat auch über pH = 8 mit Thiosulfat. Diese Reaktion ist jedoch keine eindeutige. Gleichfalls oxydiert das Perjodat—abweichend vom Jodat—das vorhandene Jodid bei ungefähr pH = 8 zu Jod

JO_3^-, JO^-, J_2, J^-
1. Anteil
JO_3^-, JO^-, J_2, J^-
Ansäuern
J_2 (ursprüngl. + ausgeschieden), J^-
Titration mit $S_2O_3^{2-}$ (Verbrauch A)
J^- (Gesamtjod), $S_4O_6^{2-}$
Titration mit Ag^+ (Verbrauch B)
AgJ, $S_4O_6^{2-}$
2. Anteil (gleichgross mit 1.)
JO_3^-, JO^-, J_2, J^-
+ $S_2O_3^{2-}$-Überschuss
JO_3^-, $S_4O_6^{2-}$ (äquivalent mit dem ursprüngl. J_2), SO_4^{2-} (äquivalent dem JO^-), J^-, $S_2O_3^{2-}$ (Überschuss)
Titration mit J_2 (Verbrauch C)
JO_3^-, $S_4O_6^{2-}$ (äquivalent mit dem ursprüngl. J_2 und dem $S_2O_3^{2-}$ Überschuss), SO_4^{2-}, J^-
Ansäuern
J_2 (äquivalent mit d. JO_3^-), $S_4O_6^{2-}$, SO_4^{2-}, J^-
Titration mit $S_2O_3^{2-}$ (Verbrauch E)
$S_4O_6^{2-}$ (äquivalent mit dem ursprüngl. J_2, dem $S_2O_3^{2-}$-Überschuss und dem JO_3^-), SO_4^{2-}, J^-
+ KCN
$S_2O_3^{2-}$ (äquivalent mit dem ursprüngl. J_2, dem $S_2O_3^{2-}$-Überschuss und dem JO_3^-), SO_4^{2-}, J^-
Titration mit J_2 (Verbrauch F)
$S_4O_6^{2-}$, SO_4^{2-}, J^-

Analyseschema 2

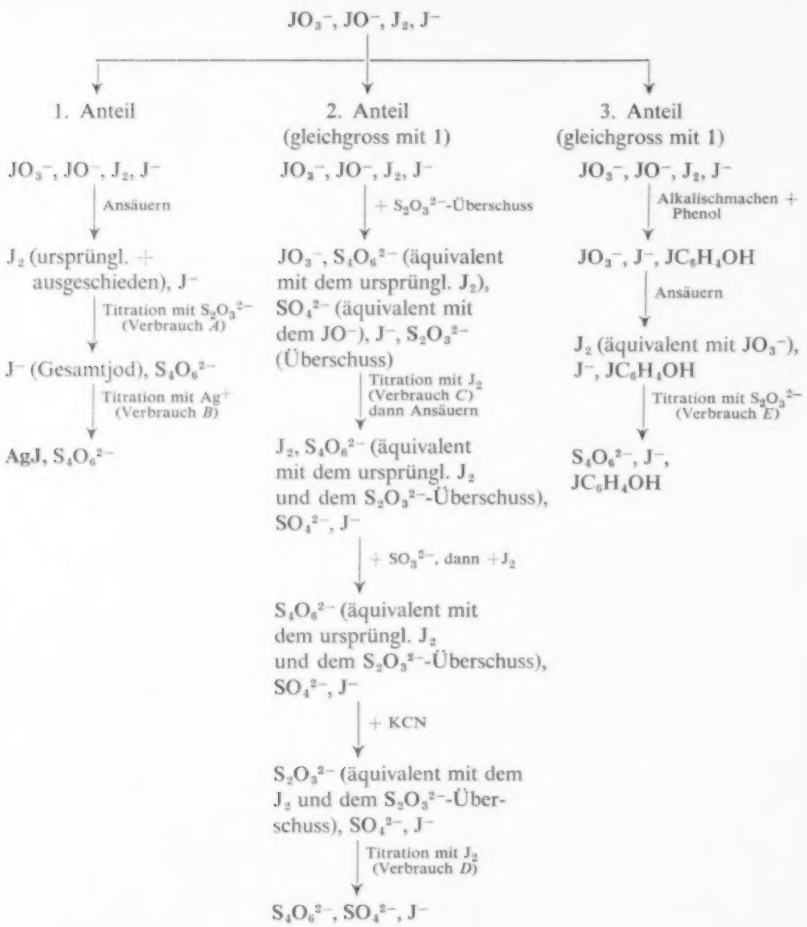
(seihe G1.4). Das Jod kann ausser den bereits erwähnten Ursachen auch deshalb mit Thiosulfat oder Arsenit nicht direkt titriert werden, weil die Perjodat–Jodid Reaktion eine Zeitreaktion ist. Während dieser Zeit geht im 0,01 n Massstabe eine nicht zu vernachlässigende Menge Jod bzw. Hypojodit in Jodat über. Mit Arsenit–Überschuss[12] kann jedoch durch Rücktitration mit Jod bei pH = 8 eine zufriedenstellende Genauigkeit erreicht werden.

Auch diese Methode beruht auf der Reaktion

$$JO_4^- + 2J^- + H_2O = JO_3^- + J_2 + 2OH^- \qquad (4)$$

da sie ja nur in Gegenwart von Jodid durchgeführt werden kann. Das vorhandene Arsenit reagiert jedoch sofort mit dem gebildeten Jod:

$$AsO_3^{3-} + J_2 + H_2O = AsO_4^{3-} + 2J^- + 2H^+ \qquad (11)$$

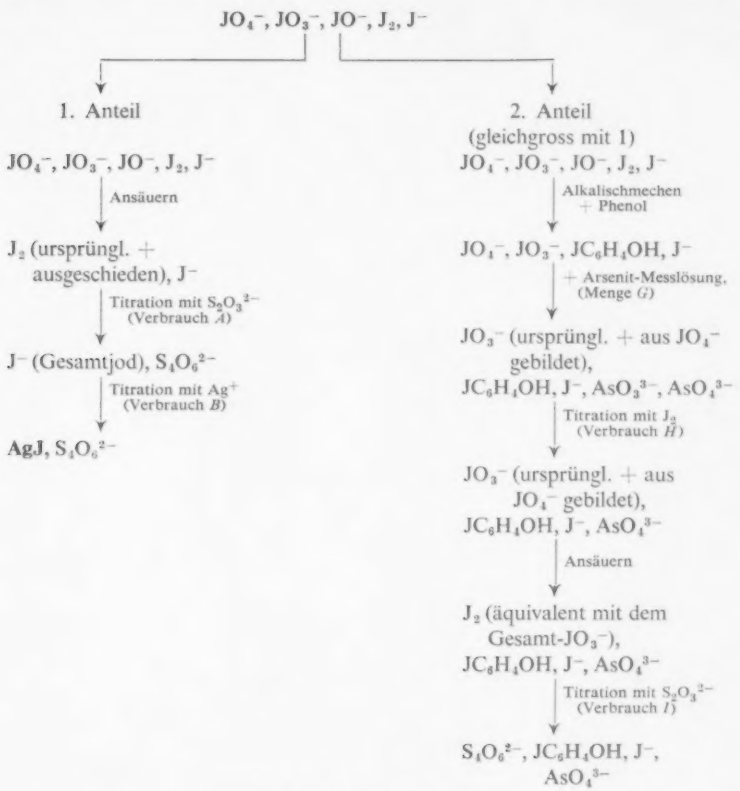

JO_3^-, JO^-, J_2, J^-
1. Anteil
JO_3^-, JO^-, J_2, J^-
Ansäuern
J_2 (ursprüngl. + ausgeschieden), J^-
Titration mit $S_2O_3^{2-}$ (Verbrauch A)
J^- (Gesamtjod), $S_4O_6^{2-}$
Titration mit Ag^+ (Verbrauch B)
AgJ, $S_4O_6^{2-}$
2. Anteil (gleichgross mit 1)
JO_3^-, JO^-, J_2, J^-
+ $S_2O_3^{2-}$-Überschuss
JO_3^-, $S_4O_6^{2-}$ (äquivalent mit dem ursprüngl. J_2), SO_4^{2-} (äquivalent mit dem JO^-), J^-, $S_2O_3^{2-}$ (Überschuss)
Titration mit J_2 (Verbrauch C) dann Ansäuern
J_2, $S_4O_6^{2-}$ (äquivalent mit dem ursprüngl. J_2 und dem $S_2O_3^{2-}$-Überschuss), SO_4^{2-}, J^-
+ SO_3^{2-}, dann + J_2
$S_4O_6^{2-}$ (äquivalent mit dem ursprüngl. J_2 und dem $S_2O_3^{2-}$-Überschuss), SO_4^{2-}, J^-
+ KCN
$S_2O_3^{2-}$ (äquivalent mit dem J_2 und dem $S_2O_3^{2-}$-Überschuss), SO_4^{2-}, J^-
Titration mit J_2 (Verbrauch D)
$S_4O_6^{2-}$, SO_4^{2-}, J^-
3. Anteil (gleichgross mit 1)
JO_3^-, JO^-, J_2, J^-
Alkalischmachen + Phenol
JO_3^-, J^-, JC_6H_4OH
Ansäuern
J_2 (äquivalent mit JO_3^-), J^-, JC_6H_4OH
Titration mit $S_2O_3^{2-}$ (Verbrauch E)
$S_4O_6^{2-}$, J^-, JC_6H_4OH

Analyseschema 3

Perjodat reagiert mit Phenol nicht, daher ist die Bestimmung des Perjodats auch in Gegenwart von Hypojodit (und Jod) möglich.

Diese Möglichkeit beruht gleichfalls auf der Ausnutzung der pH-Abhängigkeit der Reaktionsgeschwindigkeiten. Bei höheren pH-Werten läuft die Reaktion 4 nämlich langsam, der Prozess 10 jedoch augenblicklich ab. Bei Verminderung des pH-Wertes nimmt die Geschwindigkeit der Reaktion 4 allmählich zu, die der Reaktion 10 jedoch ab. Es erscheint hier aber allmählich auch der Prozess 11, der sich praktisch augenblicklich abspielt. Bei pH = 8 verschieben sich die Reaktionsgeschwindigkeiten noch mehr zugunsten der durch uns kontrollierbaren Reaktionen. Das in der Zeitreaktion 4 gebildete Jod reagiert nach der Gleichung 11 augenblicklich weiter, da die Reaktion zwischen Phenol und Jod bei pH = 8 bereits langsamer abläuft. Bei genügend rascher Vorbereitung ist also mit einem Perjodat–Verlust praktisch nicht zu rechnen.

Nach Titration des Arsenitüberschusses kann in der Lösung nach Ansäuern das ursprünglich vorhandene und das aus der Reduktion des Perjodats stammende Jodat jodometrisch bestimmt werden (siehe Analyseschema 4).


$JO_4^-, JO_3^-, JO^-, J_2, J^-$
1. Anteil
$JO_4^-, JO_3^-, JO^-, J_2, J^-$
Ansäuern
J_2 (ursprüngl. + ausgeschieden), J^-
Titration mit $S_2O_3^{2-}$ (Verbrauch A)
J^- (Gesamtjod), $S_4O_6^{2-}$
Titration mit Ag^+ (Verbrauch B)
AgJ, $S_4O_6^{2-}$
2. Anteil (gleichgross mit 1)
$JO_4^-, JO_3^-, JO^-, J_2, J^-$
Alkalischmechen + Phenol
$JO_4^-, JO_3^-, JC_6H_4OH, J^-$
+ Arsenit-Messlösung, (Menge G)
JO_3^- (ursprüngl. + aus JO_4^- gebildet), $JC_6H_4OH, J^-, AsO_3^{3-}, AsO_4^{3-}$
Titration mit J_2 (Verbrauch H)
JO_3^- (ursprüngl. + aus JO_4^- gebildet), $JC_6H_4OH, J^-, AsO_4^{3-}$
Ansäuern
J_2 (äquivalent mit dem Gesamt-JO_3^-), $JC_6H_4OH, J^-, AsO_4^{3-}$
Titration mit $S_2O_3^{2-}$ (Verbrauch I)
$S_4O_6^{2-}, JC_6H_4OH, J^-, AsO_4^{3-}$

Analyseschema 4

Die Summe des Hypojodits und des elementaren Jods kann aus der jodometrischen Bestimmung der Gesamtmenge der oxydierenden Stoffe berechnet werden. Da das obenerwähnte System auch vorübergehend nur bei höheren pH-Werten bestehen kann, ist es zweckmässig, die Ergebnisse in Hypojodit–Jod anzugeben. Die getrennte Bestimmung der beiden Komponenten ist wegen der Perjodat–Thiosulfat Reaktion, nach den früher besprochenen Prinzipien nicht durchführbar.

Auf Grund unserer Untersuchungen wurde das in seinen Verbindungen in verschiedenen Oxydationszuständen vorliegende Jod nebeneinander nach weiter unten ausführlich beschriebenen Methoden bestimmt. Es muss ausdrücklich darauf hingewiesen werden, dass nach Abmessen der einzelnen Anteile der zu untersuchenden Lösung zuerst diejenigen Operationen auszuführen sind, welche die besonders labilen Gleichgewichte, bzw. der Verschiebung dieser vorbeugen. Diese Operationen sind das Hinzufügen von Phenol und Lauge (im Abschnitt II. bzw. III) das von Thiosulfat (im Abschnitt I. und II) endlich das Hinzufügen von Arsenit (im Abschnitt III). Wir möchten dabei vorausschicken, dass die nacheinanderfolgenden Operationen kontinuierlich, also ohne Unterbrechung der Reihe nach durchgeführt werden müssen, falls eine Wartezeit nicht ausdrücklich vorgeschrieben ist. Dies ist deshalb notwendig, weil bei einem Grossteil der Fälle die Differenzen zwischen den Reaktionsgeschwindigkeiten zu analytischen Zwecken ausgenützt werden.

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TABELLE I. BESTIMMUNG VON PERJODAT, JODAT, HYPOJODIT, JOD UND JODID NEBENEINANDER

Nr.	Einwaage, *mg* (in Jod ausgedrückt)					Verbrauch, *ml*									Gefunden, *mg* (in Jod ausgedrückt)					Gesamtmenge Jod, *mg*	
	JO_4^-	JO_3^-	OJ^-	J_2	J^-	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	JO_4^-	JO_3^-	OJ^-	J_2	J^-	berechnet	gemessen
I						15,46	5,65	5,86	—	6,18	7,64	—	—	—	—	1,31	3,86	4,11	26,6		35,8
	—	1,27	3,95	4,15	26,5	15,44	5,62	5,70	—	6,08	7,53	—	—	—	—	1,28	3,85	4,16	26,4	35,87	35,6
						15,45	5,64	5,81	—	6,11	7,58	—	—	—	—	1,29	3,86	4,11	26,5		35,7
						15,23	3,19	3,20	2,17	9,88	—	—	—	—	—	2,09	2,68	1,45	14,0		20,2
II	—	2,11	2,66	1,44	13,9	15,23	3,17	3,15	2,14	9,90	—	—	—	—	—	2,09	2,68	1,43	13,9	20,11	20,1
						15,21	3,17	3,18	2,15	9,87	—	—	—	—	—	2,08	2,66	1,42	13,9		20,0
						31,14	5,75	—	—	—	—	5,05	2,42	18,17	1,67	2,17	6,57	—	26,0		36,4
III	1,71	2,15	6,35	—	26,1	31,13	5,73	—	—	—	—	5,05	2,40	18,21	1,68	2,17	6,56	—	25,9	36,31	36,3
						31,13	5,73	—	—	—	—	5,05	2,43	18,14	1,66	2,17	6,56	—	25,9		36,2

Zeichenerklarung:

A Verbrauch an 0,01 n Natriumthiosulfat Masslösung für alle oxydierenden Ionen
B Verbrauch an 0,05 n Silbernitratlösung für das gesamte Jodid nach Reduktion
C Nach Reduktion mit Natriumthiosulfat für den Überschuss bei pH = 8 verbrauchte 0,01 n Jodlösung
D Nach Reduktion des bei der vorangehenden Messung gebildeten Tetrathionats verbrauchte 0,01 n Jodlösung
E Für das Jodat verbrauchte 0,01 n Natriumthiosulfatlösung
F Nach Reduktion des bei den Titrationen *C* und *E*, sowie bei der Jod-Thiosulfat Reaktion gebildeten Tetrathionats verbrauchte 0,01 n Jodlösung
G Zugegebene Menge 0,01 n arsenige Säure
H Für den Überschuss der arsenigen Säure bei pH = 8 verbrauchte 0,01 n Jodlösung
I Für das ursprünglich vorhandene und bei der Reduktion des Perjodats gebildete Jodat verbrauchte 0,01 n Natriumthiosulfatlösung

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Ein Teil unserer experimentellen Ergebnisse ist auch tabellarisch dargestellt. Die in der Rubrik "Einwaage, *mg*" der Tabelle angeführten Daten sind teils effektive Einwaagen, teils aus getrennten Messungen berechnete Werte, die auch auf Grund der Skrabalschen[1] Daten kontrolliert wurden. Die zu den Modellversuchen gebrauchte Lösung wurde aus drei Stammlösungen (0,01 n Perjodat-, Jodat-bzw. 0,01 n Jodid–Jod–Hypojodit–Lösungen) unmittelbar vor der Ausführung der Analyse vermengt. Die Mengenverhältnisse der Jodid–Jod–Hypojodit–Lösung müssten aus den Einwaagen auf Grund der Skrabalschen Daten rechnerisch ermittelt werden.

BESCHREIBUNG DER VERFAHREN

Reagenzien

Natriumthiosulfatlösung, 0,01 n
Kaliumjodidhaltige Jodlösung, 0,01 n
Arsentrioxydlösung (neutral), 0,01 n
Silbernitratlösung, 0,05 n
Kartoffelstärkelösung, 1% ige mit 0,1% Salicylsäure abgebaute und konservierte
p-Äthoxychrisoidinlösung, 0,2% ige in 96% igem Alkohol
Phenolphthaleinlösung, 0,1% ige
Perchlorsäurelösung, 20% ige
Kohlendioxyd (aus Stahlflasche)
Natriumhydroxydlösung, 20% ige
Natriumhydroxydlösung, ca. 0,1% ige
Kaliumcyanidlösung, 5% ige
Phenollösung, 1% ige
Formaldehydlösung, 5% ige
Natriumsulfitlösung, 1% ige
Die Reagenzien waren analytisch rein.

I. *Bestimmung von Jodid-Jod, elementarem Jod, Hypojodit- und Jodat-Jod, wenn relativ wenig Jodat und relativ viel Jodid vorhanden ist*

Ein genau gemessener 20–40 mg Gesamtjod entsprechender Anteil der zu untersuchenden Lösung wird in einem 100 ml fassenden Erlenmeyerkolben mit eingeschliffenem Glasstopfen mit so viel Perchlorsäure angesäuert, dass die Lösung auf Perchlorsäure etwa 0,1 normal ist. Nach 10 Minuten wird das ursprüngliche und das ausgeschiedene Jod in Gegenwart von Stärke als Indikator mit Thiosulfatlösung titriert. Die Zahl der verbrauchten ml 0,1 n $Na_2S_2O_3$ wird mit *A* bezeichnet.

Die austitrierte Lösung giesst man nun in einen geräumigeren Kolben, verdünnt auf ca. 200 ml und neutralisiert genau in Gegenwart von 1–2 Tropfen p-Äthoxychrysoidinlösung zuerst mit 20% iger Natronlauge, dann mit Perchlorsäure und schliesslich mit verdünnter Natronlauge. Es werden nun weitere 8–10 Tropfen p-Äthoxychrysoidinlösung zugegeben und das Jodid langsam und unter ständigem Rühren mit 0,05 n Silbernitratlösung titriert. Das p-Äthoxychrysoidin als Adsorptionsindikator schlägt im Endpunkt von himbeerrot auf gelb um. Der Verbrauch wird mit *B* bezeichnet.

In einem anderen, gleich grossen Anteil der Lösung lässt man nun rasch 1/2–1/6 des Volumens *A* der Thiosulfatlösung einlaufen. (Die notwendige Menge Thiosulfat wird nach der Menge Jodat, der relativen Menge Jod bzw. Hypojodit bemessen). Nach Vermischen werden 1–3 Tropfen Phenolphthaleinlösung zugegeben, dann wird so lange CO_2-Gas durch die Lösung geleitet, bis diese eben entfärbt ist und schliesslich in Gegenwart von 5–10 Tropfen Stärkelösung der Thiosulfatüberschuss mit Jodlösung titriert. Der Verbrauch wird mit *C* bezeichnet.

Man tropft nun Perchlorsäure zum Reaktionsgemisch bis das Brausen der Lösung nachlässt und dann noch so viel, bis der pH-Wert zwischen 1 und 2 liegt. Nach etwa 10 Minuten wird das ausgeschiedene Jod mit Thiosulfat titriert. Der dem Jodatgehalt proportionale Verbrauch wird mit *E* bezeichnet.

Die Lösung wird hierauf mit Natronlauge neutralisiert und noch 2 ml überschüssige Natronlauge, sowie 1–2 ml Kaliumcyanidlösung zugegeben. Man stellt die Lösung für 15 Minuten beiseite. Während dieser Zeit spielt sich die Reaktion 8 ab, dann werden zur Bindung des Cyanidüberschusses 1–2 ml Formaldehydlösung zugegeben. Nach einigen Minuten wird die Lösung schwach angesäuert

und das gebildete Thiosulfat mit Jodlösung titriert. Der Verbrauch der Jodlösung wird mit F bezeichnet.

Die für die einzelnen komponenten verbrauchten ml der Masslösungen können folgendermassen berechnet werden (siehe Analyseschema 2):

Der Verbrauch E ist unmittelbar dem Jodat-Jod proportional. Das Äquivalentgewicht ist im Sinne der Gleichung 3 ein Sechstel des Atomgewichts des Jodat-Jods.

Für das Jodat-Jod werden also E ml 0,01 n Thiosulfatlösung verbraucht.

Der ursprüngliche Jodgehalt kann aus dem Ergebnis der Tetrathionat-Titration (F) berechnet werden, unter Berücksichtigung dessen, dass in der Reaktion 8 aus einem Tetrathionat ein Thiosulfat gebildet wird (das Äquivalenzverhältnis ist also unterschiedliches von dem in der Reaktion 6), und dass sich sowohl bei der Thiosulfatmessung (C) als auch bei der Jodatmessung (E) Tetrathionat bildet.

Für das elementar vorhandene Jod werden also

$$[2F - (E + C)] = a$$

ml 0,01 n Thiosulfatlösung verbraucht. (Der Einfachheit halber wird dieser Wert mit a bezeichnet).

Das Äquivalentgewicht ist das Atomgewicht (siehe Gl. 6) des Jods.

Die Menge Hypojodit-Jods kann aus der für die Gesamtmenge des elementaren Jods bzw. der Jodverbindungen mit den Oxydationszahlen 0, +I, +V verbrauchten Messlösung (A) nach Abzug der für das Jodat und Jod verbrauchten Volumina berechnet werden.

Für das Hypojodit-Jod wurden also

$$[A - (E + a)] = b$$

0,01 n Thiosulfatlösung verbraucht.

Das Äquivalentgewicht des Hypojodit-Jods ist die Hälfte seines Atomgewichtes (siehe Gl. 1).

Schliesslich erhält man die ml der ursprünglichen Menge Jodid-Jod entsprechende Messlösung, wenn man aus dem Verbrauch B die ml Messlösung, welche zur Bestimmung des freien sowie des Hypojodit- bzw. Jodat-Jods verbrauchten Messlösung nach entsprechender Umrechnung, unter Berücksichtigung, dass die Silbernitratlösung 0.05 normal ist, in Abzug bringt.

Wenn man auf Grund der Reaktion

$$JO_3^- + 6e \rightarrow J^- \qquad (12)$$

die zur Bestimmung des Jodat-Jods verbrauchten ml Thiosulfatlösung in $AgNO_3$ Lösung umrechnen wünscht, so werden die ml Thiosulfatlösung mit 6 dividiert. So ist die Jodid-Jodäquivalente des aktuellen Jodat-Jods in 0,05 n $AgNO_3$ Masslösung ausgedrückt $1/30 = 0{,}0333$.

Die zur Messung des elementar vorhandenen Jods verbrauchten ml 0,01 n Thiosulfatlösung werden schliesslich durch Multiplizieren mit 0,2 in 0,05 $AgNO_3$-Lösung umgerechnet, da die Jodmengen bei der jodometrischen und der beschriebenen argentometrischen Messungen äquivalent sind.

Dem Hypojodit-Jod äquivalente Menge Thiosulfatlösung ist im Sinne der Gleichung

$$JO^- + 2e \rightarrow J^- \qquad (13)$$

die Hälfte des tatsächlichen Masslösung-Verbrauches. Bei Umrechnung des letzteren in 0,05 n $AgNO_3$-Lösung muss demgemäss mit 0,1 multiplizieren.

Für den ursprünglichen Jodid-Jodgehalt wurde also $[B - (0{,}0333\,E + 0{,}2\,a + 0{,}1\,b)]$ ml 0,05 n $AgNO_3$-Lösung verbraucht.

Auf Grund obiger Darlegungen entspricht 1 ml 0,01 n Natriumthiosulfatlösung
0,2115 mg Jod im Oxydationszustand +V (Jodat);
0,6346 mg Jod im Oxydationszustand +I (Hypojodit); bzw.
1,2692 mg Jod im Oxydationszustand 0 (elementares Jod.)
1 ml 0,05 n Silbernitratlösung entspricht 6,346 mg Jod im Oxydationszustand −I (Jodid.)

II. *Bestimmung von Jodid-Jod, elementarem Jod, Hypojodit- und Jodat-Jod nebeneinander, wenn grössere Menge Jodat, und relativ viel Jodid vorhanden ist*

Im ersten Anteil der 20–40 mg Gesamtjod entsprechenden, genau eingemessenen Lösung werden die Menge des Jods im Oxydationszustand O, +I, +V und der gesamte Jodgehalt (letzterer in Form von Jodid) ebenso bestimmt wie bei der vorangehend im Abschnitt I. beschriebenen Methode. Die verbrauchten ml Masslösung werden auch hier mit A bzw. B bezeichnet.

Zum zweiten (gleich grossen) Anteil der Lösung wird gleichfalls ein Thiosulfatüberschuss zugegeben und der Überschuss bei pH = 8 mit Jodlösung titriert. Dieser Wert wird mit *C* bezeichnet.

Die Lösung wird nun angesäuert, und das gebildete Jod mit Sulfitlösung reduziert. Der Sulfitüberschuss wird mit 0,01 n Jodlösung gebunden. Man bestimmt hierauf den Tetrathionatgehalt der Lösung mit der bereits beschriebenen Cyanid-Methode. Der Verbrauch an 0,01 n Jodlösung wird mit *D* bezeichnet.

In einem dritten, gleich grossen aliquoten Teil wird schlieslich der Jodatgehalt nach folgender Methode bestimmt:

Man macht die Lösung mit 1 ml 20% iger Natronlauge alkalisch, und versetzt unverzüglich mit 1–2 ml Phenollösung. Nun wird auf 50 ml verdünnt und in Gegenwart von einigen Tropfen Phenolphthaleinlösung bis zur Entfärbung Kohlendioxyd eingeleitet. Man säuert hierauf mit so viel Perchlorsäure an, dass diese nicht nur die Hydrocarbonate zersetzt, sondern auch der Säuregehalt auf etwa 0,1 n eingestellt wird. Nach 10 Minuten wird die mit dem Jodat äquivalente Jodmenge mit Thiosulfat titriert. Der Verbrauch wird mit *E* bezeichnet. Der Gang der Analyse ist im Analyseschema 3 gezeigt.

Die für die einzelnen Komponenten verbrauchten Mengen der Masslösungen werden nach folgenden Formeln berechnet:

Für das Jodat: *E* ml;

für das Jod (da sich bei der Reduktion des Jodats kein Tetrathionat gebildet hat, siehe Gl. 9): $[2D - C] = c$ ml;

und für das Hypojodit (auf Grund der im ersten Kapitel beschriebenen Überlegungen): $[A - (E + c)] = d$ ml 0,01 n $Na_2S_2O_3$-Lösung.

Dem ursprünglichen Jodidgehalt der Lösung entspricht $[B - (0{,}0333\,E + 0{,}2\,c + 0{,}1\,d)]$ ml 0,05 n $AgNO_3$-Lösung.

Die Äquivalentgewichte sind die gleichen wie die im Abschnitt I angegeben worden sind.

III. *Bestimmung von Jodid-Jod, elementarem Jod, Hypojodit-, Jodat-, und Perjodat-Jod nebeneinander, wenn relativ viel Jodid-Jod verhanden ist*

Im ersten, 20–40 mg Gesamtjod entsprechenden, genau gemessenen aliquoten Teil werden die Messungen mit den Messwerten *A* bzw. *B* wie in den vorangehendenen Abschnitt II. bzw. I. durchgeführt.

Ein zweiter gleich grosser Lösungsanteil wird mit 1 ml 20% iger Natronlauge alkalisch gemacht und unverzüglich mit 1–2 ml Phenollösung, sowie mit einer genau gemessenen, dem erwarteten Perjodatgehalt entsprechenden Menge einer 0,01 normalen Lösung von arseniger Säure versetzt. Die Menge der arsenigen Säure wird mit *G* bezeichnet. Man gibt nun einige Tropfen Phenolphthalein hinzu und leitet bis zur Entfärbung CO_2 ein. Nach 15 Minuten wird der Überschuss der arsenigen Säure auf Stärke als Indikator mit 0,01 n Jodlösung titriert (*H*). Die Lösung wird auf etwa pH = 1 angesäuert und nach 15 Minuten wird das durch den ursprünglichen und den bei der Reduktion des Perjodats gebildeten Jodatgehalt freigemachte Jod mit 0,01 n Thiosulfatlösung titriert. Das Ergebnis wird mit *I* bezeichnet.

Für die einzelnen Komponenten wurden folgende Mengen Masslösung verbraucht:

Die Perjodatmenge kann in Kenntnis der Mengen der Arsenitlösung (*C*) und für deren Überschuss verbrauchten Jodlösung (*H*) berechnet werden.

Für das Perjodat wurden also

$[G - H] = e$ ml 0,01 n Thiosulfatlösung äquivalente 0,01 n arsenige Säure verbraucht.

Das Äquivalentgewicht des Perjodat-Jods ist auf Grund der Reaktion 4 die Hälfte des Atomgewichts. Im Laufe dieser Reaktion bildet sich Jodat, dies muss also bei der Berechnung der für das ursprüngliche Jodat verbrauchten Lösungsmenge berücksichtigt werden. Auch muss man in Betracht ziehen, dass zwischen den Reaktionen 3 und 4 ein Äquivalenz-Unterschied besteht, daher sind dem ursprünglichen Jodat-Jodgehalt der Lösung:

$[I - 3e] = f$ ml 0,01 n Thiosulfatlösung äquivalent.

Der gemeinsamen Menge Hypojodit + elementares Jod entsprechende ml Thiosulfatlösung erhält man, wenn man aus den dem elementaren + Hypojodit-, Jodat- und Perjodat-Jod anzeigenden ml *A* die für das Jodat- und Perjodat-Jod verbrauchten ml der Messlösung in Abzug bringt.

$$[A - (f + 4e)] = \sigma \text{ ml}$$

Dem ursprünglichen Jodidgehalt der untersuchten Lösung (angenommen dass die Lösung nur Hypojodit nicht aber elementares Jod enthält und unter Berücksichtigung dessen, dass das Äquivalentgewicht des JO_4^- von dem auf Grund der Reaktion 4 berechneten auch hier abweicht) sind:

$[B - (0{,}1\,e + 0{,}0333\,f + 0{,}1\,g)]$ ml 0,05 n Silbernitratlösung gleichwertig.

Die Äquivalentgewichte für das Jod in verschiedenen Oxydationszuständen sind die gleichen, die am Ende des Abschnittes I. angegeben worden sind bzw. 1 ml 0,01 n arsenige Säure entspricht (auf Grund der Reaktionen 4 und 11) 0,6346 mg Jod im Oxydationszustand + VII (Perjodat).

Schliesslich möchten wir noch erwähnen, dass unsere Untersuchungen mit solchen Systemen durchgeführt wurden, in denen die Menge Jodid–Jods im Verhältnis zum Jod mit anderen Oxydationszahlen im Überschuss vorlag. Ist wenig Jodid vorhanden, so muss vor den oxydimetrischen Titrationen eine entsprechende Jodidmenge in das System eingetragen werden. Das Jodid–Jod bzw. das Gesamtjod lässt sich in einem separat vorbereiteten (reduzierten)Lösungsanteil bestimmen.

Summary—A system consisting of iodide, iodine, hypo-iodite, iodate and periodate is labile, and has a transient existence at higher pH values. Periodate may be reduced, after decomposition of hypo-iodite, with phenol in an excess of arsenious acid, the excess of which is back-titrated. The iodate, after reduction of iodine and hypo-iodite by means of phenol, is determined iodometrically. In the presence of periodate, the quantity of iodate formed is equivalent to the periodate. The total quantity of hypo-iodite and iodine is calculated from the difference of the iodometric measurements (with and without phenol). After determination of the total amount of oxidising substance, the total amount of iodide can be measured with silver nitrate using *p*-ethoxychrysoidine as adsorption indicator. In the absence of periodate, elementary iodine along with hypo-iodite is determined using the same principles. Thiosulphate is oxidised by hypo-iodite to sulphate, but by iodine to tetrathionate. The latter can be determined by the procedure of Kurtenacker and Fritsch.

Résumé—Un système composé d'iodure, d'iode, d'hypoiodite, d'iodate et de periodate est labile et peut exister seulement aux fortes valeurs de pH sous contrôle. Certains auteurs réduisent le periodate, après décomposition de l'hypoiodite au moyen du phénol, avec un excès d'acide arsénieux, et titrent l'excès. L'iodate, après réduction de l'iode et de l'hypoiodite au moyen du phénol, est dosé par iodométrie. La quantité totale d'hypoiodite et d'iode est calculée d'après la différence des titres iodométriques (avec ou sans phénol). Après dosage de la quantité totale d'oxydant, l'iode total peut être dosé au moyen du nitrate d'argent, en utilisant la p-éthoxychrysoidine comme indicateur d'adsorption.

En l'absence de periodate, l'iode élémentaire en présence d'hypoiodite est dosé d'après le principe que le thiosulfate est oxydé en sulfate par l'hypoiodite, et en tétrathionate par l'iode. Cette dernière réaction peut être réalisée en utilisant le procédé de Kurtenacker et Fritsch. Les résultats sont satisfaisants.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—III

ALUMINIUM

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Summary—A study has been made of the precipitation of aluminium from homogeneous solution with 8-acetoxyquinoline. The use of 8-acetoxyquinoline results in an aluminium precipitate with superior physical characteristics as compared to that produced in the conventional manner with 8-hydroxyquinoline. A separation of 25-mg quantities of aluminium from 300 mg of magnesium or 1000 mg of calcium can easily be made.

THE precipitation of aluminium from homogeneous solution as the 8-hydroxyquinolate was accomplished by Stumpf[1] who used urea to raise the pH of an acid solution containing urea and 8-hydroxyquinoline. 8-Acetoxyquinoline can also be used as a source of 8-hydroxyquinoline to precipitate metal 8-hydroxyquinolates from homogeneous solution.[2,3] The present paper describes the use of 8-acetoxyquinoline for the precipitation of aluminium in an acetate-buffered solution at pH 5.

PROCEDURE

Dissolve 1·0 g of 8-acetoxyquinoline in 25 ml of 1:1 acetic acid in a 250-ml beaker. Add immediately a solution containing 3 to 25 mg of aluminium and dilute to approximately 150 ml with distilled water. Adjust the pH slowly to 5·0 using filtered 1:1 ammonium hydroxide. Dilute the solution to 200 ml, cover the beaker with a watch-glass, and place on an electric hot-plate so regulated that the solution may be raised to approximately 50° and held at this temperature for 3 hr. Cool to room temperature and filter through a medium porosity filtering crucible, transferring and washing the precipitate with about 100 ml or less of cold water. Dry at 135 ± 5° for 1 hr and weigh as $Al(C_9H_6NO)_3$; the gravimetric factor is 0·0587.

REAGENTS

Aluminium: An aluminium solution was prepared by dissolving the high-purity metal (>99·9% aluminium) in hydrochloric acid and diluting. The standard value was obtained by precipitation of the aluminium with ammonium hydroxide.[4]

Calcium: Reagent grade $Ca(NO_3)_2 \cdot 4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Magnesium: Reagent grade $Mg(NO_3)_2 \cdot 6H_2O$ (General Chemical Company, New York).

8-*Hydroxyquinoline:* A solution was prepared by adding 5 ml of glacial acetic acid to 2·5 g of the reagent (Matheson, Coleman, and Bell Division of Matheson Company, East Rutherford, New Jersey); after warming to dissolve the reagent, the solution was diluted to 90 ml with warm water, cooled, filtered to remove solid matter, and then diluted to 100 ml.

8-*Acetoxyquinoline:* This reagent was prepared by the method of Salesin and Gordon[2] with slight modification, *i.e.*, instead of a 3-fold excess of acetic anhydride only a 20% excess was used.

EXPERIMENTAL

Preliminary investigations were made to determine the appropriate concentrations of reagents, the temperature of reaction, and the pH, which would result in the quantitative precipitation of aluminium 8-hydroxyquinolate in a form with desirable physical characteristics.

No precipitate could be obtained at pH 4·0, heating the solution, with 8-acetoxyquinoline present, for three hours at 45°. At pH 4·5, aluminium 8-hydroxyquinolate precipitated in the form of spherical aggregates at temperatures between 25 and 75°; above 75° the physical appearance of the precipitate began to change and stubby needles, with slight curvature, were formed between 85° and the boiling

TABLE I.—SEPARATION AND DETERMINATION OF ALUMINIUM BY PRECIPITATION AS THE 8-HYDROXYQUINOLATE

Number	1	2	3	4	5	6	7	8	9	10
Method of precipitation	Conventional	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS
Modifications in precipitation procedure	a	b c	b	b	d	d	d	d	d	d
Diverse element taken, *mg*	none	none	none	none	none	none	none	Mg 100	Mg 300	Ca 1000
Aluminium taken, *mg*	25·67	25·67	10·27	25·67	3·08	10·27	25·67	25·67	25·67	25·67
Difference, *mg*	−0·11 −0·01 +0·01	−0·19 −0·16 −0·18	−0·07 −0·06 −0·02 −0·03 −0·03	0·00 +0·02 0·00	+0·10 +0·10 +0·01	+0·03 −0·02 −0·03	+0·02 +0·05 +0·03 +0·01 +0·02 +0·07 +0·06	+0·09 +0·05 +0·08	+0·11 +0·05 +0·10	+0·01 +0·06 +0·03

a. Aluminium precipitated by the method of Knowles.[7]
b. The initial pH of the solution was 4·5.
c. Transfer of the precipitate was made with filtrate as described by Takiyama *et al.*[3]; 0·8 g of 8-acetoxyquinoline used instead of customary 1-g amount.
d. The initial pH of the solution was 5·0.

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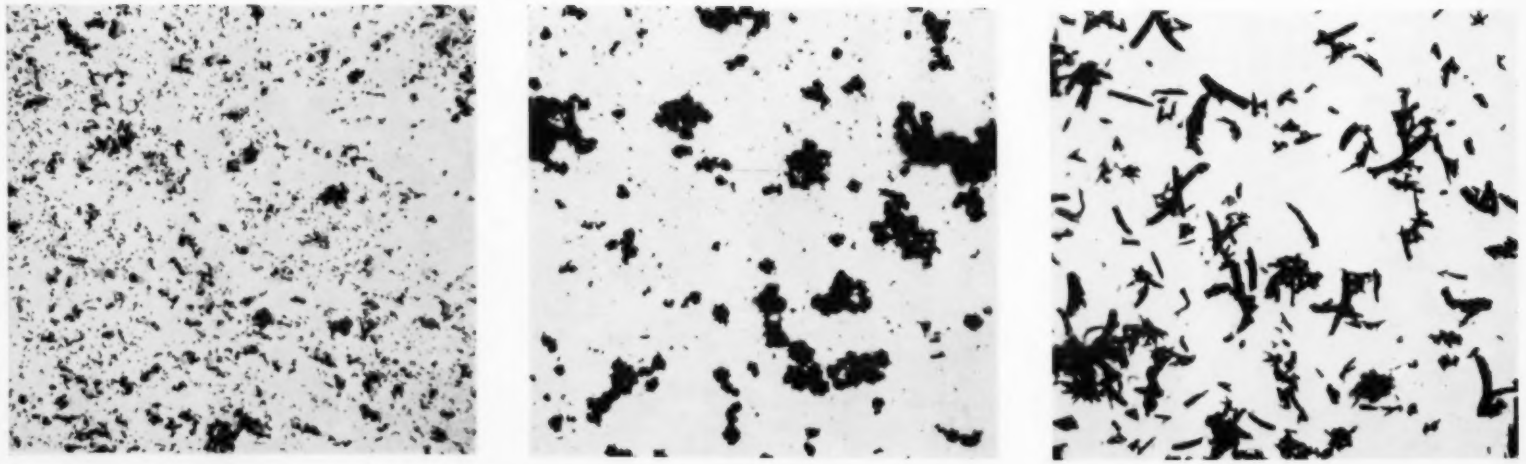

FIG. 1.—Photomicrographs of aluminium 8-hydroxyquinolate (all photomicrographs are at same magnification)
a, left panel: conventional method of precipitation.
b, centre panel: prepared by PFHS as described in procedure (t = 50°).
c, right panel: prepared by PFHS as described in procedure, but at boiling temperature.

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point. In all cases the precipitate was of better physical form than that obtained by a direct method of addition of 8-hydroxyquinoline. Only spherical aggregates were obtained within the pH range 4·5 to 8·0, at 25 to 45°. Above pH 7·8, precipitation of the aluminium with 8-acetoxyquinoline occurred almost instantly.

The best results for analytical purposes were obtained by using 1·0 g of 8-acetoxyquinoline (approximately twice the stoichiometric quantity required for 25 mg of aluminium), heating the solution for 3 hr at 50°, and buffering at a pH of 5·0. Almost equally satisfactory results were obtained at pH 4·5.

Photomicrographs of several aluminium 8-hydroxyquinolate precipitates are shown in Fig. 1.

RESULTS AND DISCUSSION

Table I shows that satisfactory results can be obtained with from 3 to 25 mg of aluminium using the procedure given. Results obtained at pH 4·5 are also given although they appear to be slightly low in some cases.

With an initial pH of 5·0, the buffer capacity of the solution is such that the final pH will not vary more than $\pm$0·2 pH unit.

Spectrophotometric determination of the aluminium[5] in the filtrate and wash showed that the combined solubility loss is quite small, *i.e.*, less than 0·02 mg.

According to Goto,[6] calcium begins to precipitate at pH 6·11 and magnesium at pH 6·7 so that a good separation of aluminium from calcium and magnesium can be expected. The results of Table I show that 25 mg of aluminium can easily be separated from at least up to 1000 mg of calcium and up to 300 mg of magnesium.

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Zusammenfassung—Eine Studie der Fällung von Aluminium mit 8-Acetoxychinolin aus homogener Lösung wurde durchgeführt. Die Niederschläge zeigen erheblich bessere physikalische Eigenschaften, als Fällungen, die mit Oxin erhalten wurden. 25 mg Aluminium können leicht von 300 mg Magnesium und 1000 mg Calcium getrennt werden.

Résumé—Les auteurs ont étudié la précipitation de l'aluminium par la 8-acétoxyquinoléine en solution homogène. La 8-acétoxyquinoléine est utilisée, car le précipité d'aluminium a des caractéristiques physiques supérieures à celles obtenues dans la méthode ordinaire avec la 8-hydroxyquinoléine. Une séparation de 25 mg. d'aluminium d'une part, et de 300 mg. de magnésium ou 1000 mg. de calcium d'autre part peut facilement être réalisée.

Authors' Note: During the time that the present investigation was being completed, Howick and Trigg also reported on the precipitation of aluminium from homogeneous solution with 8-acetoxyquinoline, at the American Chemical Society meeting, New York, September 11–16, 1960. These authors also reported a method of synthesis of 8-acetoxyquinoline which differs in several respects from that described previously by Salesin and Gordon.[2] Although the latter paper, published in March 1960, mentions the precipitation of aluminium with 8-acetoxyquinoline, consultation between one of us (L.G.) and Professor Howick indicates that both investigations were independently conceived.

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ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—II

HIGHLY SELECTIVE DETERMINATION OF ZINC WITH DITHIZONE

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Summary—Zinc has been determined by a single extraction in the form of a complex with dithizone, in amounts of the order of 10^{-6} to 10^{-8} g/ml with an average precision of $\pm 1{\cdot}0\%$, and in amounts of the order of 10^{-9} g/ml with an average precision of $\pm 15\%$. In the analysis even a large excess of metals which form extractable complexes with dithizone does not interfere. The method is very simple and rapid, for it consists of a single extraction of the solution to be analysed and measurement of the activity of the extract obtained. The procedure developed is more precise and sensitive than the colorimetric determination of zinc with dithizone.

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INTRODUCTION

IN a preceding paper[1] the theoretical foundation was given for the determination of trace amounts of metals by extraction followed by isotopic dilution analysis. From this work it was concluded that in each case an element may be selectively determined, in the form of an extractable complex, which has the highest value of the constant of the extraction process, K. The selective determination of such an element does not present any great difficulties. To prove the possibility of using this method under more difficult conditions the determination of zinc has been chosen, because in this case a masking agent must be used to attain selectivity.[1] The determination of trace amounts of zinc is also important from a practical point of view in ascertaining the purity of semi-conductor materials.

EXPERIMENTAL

Apparatus

A scintillation counter with well-type NaI(Tl) crystal.
A pH-meter Radiometer TTTl (Copenhagen).
A mechanical shaker, glass test-tubes with ground stopper, volume 25 ml.

Reagents

Distilled water: Twice-distilled, free from zinc. Purity was controlled by a colour reaction with dithizone.

Carbon tetrachloride: A.R., twice distilled.

Dithizone: A.R.

Buffer solution: 0·1*N* ammonium chloride was purified twice by dithizone and its pH regulated by the addition of ammonia, purified twice by isothermal distillation.

Hydrochloric acid: A.R., purified by repeated distillation.

Diethanoldithiocarbamate:[2,3] Prepared by mixing 6·0 g of A.R. diethanolamine and 3·5 g of A.R. carbon disulphide in 120 ml of absolute A.R. methanol. Before each experiment 50 ml of this solution was mixed with 450 ml of ammonium chloride—ammonia buffer and purified by dithizone extraction to remove the last traces of zinc [solution (I)].

Radio-zinc solution (^{65}Zn, $T_{1/2} = 250$ days):[4] A solution of specific activity 100 mc/g of zinc was

always diluted to the necessary concentration with twice-distilled water. A solution of non-active zinc was prepared by dissolving 99·999% pure metal in the necessary amount of sulphuric acid and was diluted to the required concentration by twice-distilled water.

Procedure

To 10 ml of the analysed solution of non-active zinc (of the order of magnitude of 10^{-6} g of zinc/ml), which contained a great excess of other metals, $42{\cdot}50 \times 10^{-6}$ g of radio-zinc (y) were added. After the addition of 4 ml of solution (I) the pH of the analysed solution must reach a value of 7·5 to 8·5. If the original solution is too acid, its acidity must be decreased with ammonia free from zinc. The solution thus prepared is extracted by about 1·4 ml of 10^{-4} M dithizone solution in carbon tetrachloride. After shaking for 20 min, the organic phase is separated and the activity of 1·00 ml of the solution is measured by a scintillation counter (A_2). At the same time a solution, containing $(40\text{–}100) \times 10^{-6}$ g of radio-zinc, 4 ml of solution (I) and 1·4 ml of the same amount of dithizone solution in carbon tetrachloride, is extracted. The activity of 1·00 ml of the extract is measured by a scintillation counter (A_1). The amount of non-active zinc determined is calculated from the relation:

$$x = y\left(\frac{A_1}{A_2} - 1\right).$$

RESULTS AND DISCUSSION

In Table I the results are given of determinations carried out by the procedure described, and the errors are evaluated for the various concentration regions. At the

TABLE I.—EXTRACTION OF ZINC BY DITHIZONE
($3{\cdot}2 \times 10^{-6}$ g of Zn/ml to $3{\cdot}2 \times 10^{-9}$ g of Zn/ml[a])

Zinc taken, μg (X)	Active zinc added, μg (y)	Activity of extracts[b]		Zinc found, μg (x)	Deviation from mean, μg (Δ)	Other metals present, μg	Deviations[c]
		A_1	A_2				
32·65	42·50	79·788	44·994	32·90	+0·51	0	$\sigma = 32{\cdot}39$
		79·402	45·206	32·16	−0·23	1000 Cu^{2+}	$\delta = \pm 0{\cdot}174 = \pm 0{\cdot}54\%$
		79·402	45·048	32·41	+0·06	1000 Hg^{2+}	$\sigma - X = -0{\cdot}26 = -0{\cdot}8\%$
		79·402	45·217	32·11	−0·28	500 Fe^{2+}	
		81·068	45·674	32·96	+0·57	1000 Co^{2+}	
		81·068	45·626	33·08	+0·69	500 Cu^{2+}	
		81·410	46·918	31·30	−1·09	500 Sn^{2+}	
		81·410	46·404	32·10	−0·29	1000 Bi^{3+}	
		81·410	46·109	32·56	−0·17	1000 Pb^{2+}	
		79·518	45·524	31·70	−0·69	0	
		79·518	44·777	32·00	+0·59	0	
3·265	4·250	47·909	26·846	3·345	+0·026	100 Pt^{4+}	$\sigma = 3{\cdot}319$
		47·909	26·654	3·331	+0·012	100 Cu^{2+}	$\delta = \pm 0{\cdot}003 = \pm 0{\cdot}9\%$
		46·476	25·842	3·388	+0·069	500 Ni^{2+}	$\sigma - X = +0{\cdot}051 = +1{\cdot}8\%$
		46·476	26·160	3·300	−0·019	300 Cu^{2+}	
		43·857	24·691	3·300	−0·019	100 Co^{2+}	
		49·239	27·082	3·469	−0·150	500 Hg^{2+}	
		49·239	28·081	3·216	−0·103	500 Cd^{2+}	
		49·239	28·298	3·150	−0·169	500 Pb^{2+}	
		46·476	25·885	3·380	+0·061	1000 Cu^{2+}	
0·3265	0·4250	64·000	37·000	0·3108	−0·0235	50 Ag^{1+}	$\sigma = 0{\cdot}3343$
		64·000	35·100	0·3503	+0·0160	50 Bi^{3+}	$\delta = \pm 0{\cdot}00523 = \pm 1{\cdot}57\%$
		64·000	36·270	0·3250	−0·0093	50 Fe^{2+}	$\sigma - X = +0{\cdot}0078 = +2{\cdot}4\%$
		64·000	36·440	0·3210	−0·0133	50 As^{3+}	
		32·570	18·225	0·3340	−0·0003	50 Cd^{2+}	
		24·951	13·990	0·3366	+0·0023	50 Pb^{2+}	
		24·951	13·740	0·3469	+0·0126	50 Cu^{2+}	
		23·600	12·930	0·3501	+0·0158	50 Hg^{2+}	
0·03265	0·2125	7·880	7·020	0·0269	−0·0134	5 Ni^{2+}	$\sigma = 0{\cdot}0403$
		7·880	7·100	0·0234	−0·0169	5 Cu^{2+}	$\delta = \pm 0{\cdot}0061 = \pm 15{\cdot}2\%$
		7·470	6·400	0·0353	−0·0050	10 Co^{2+}	$\sigma - X = 0{\cdot}0077 = +19\%$
		7·470	5·870	0·0580	+0·0177	10 Hg^{2+}	
		7·470	5·865	0·0580	+0·0177	0	

[a] Volume of analysed solution in all experiments listed in Table was 10 ml.
[b] In the range 3×10^{-6} g of Zn/ml, $C_{HA} = 1 \times 10^{-4}$ M and A_1, A_2 expressed in cpm.
3×10^{-7} g of Zn/ml, $C_{HA} = 5 \times 10^{-5}$ M and A_1, A_2 expressed in cpm.
3×10^{-8} g of Zn/ml, $C_{HA} = 0{\cdot}5$ to $1{\cdot}0 \times 10^{-5}$ M and A_1, A_2 expressed in cp 5 min.
3×10^{-9} g of Zn/ml, $C_{HA} = 2 \times 10^{-6}$ M and A_1, A_2 expressed in cp 5 min.

[c] $\sigma = \dfrac{\sum_{x=1}^{x=n} X}{n}$, $\quad \delta = \pm\sqrt{\dfrac{\Sigma\Delta^2}{n(n-1)}}$

same time the amounts of added active zinc and dithizone concentrations c_{HA} are given. The dithizone concentration is always lower than would correspond to the stoichiometric amount of zinc present.

The influence of pH on the extraction of zinc by a 10^{-4} *M* solution of dithizone in carbon tetrachloride is shown in Fig. 1. In these experiments the volume of the

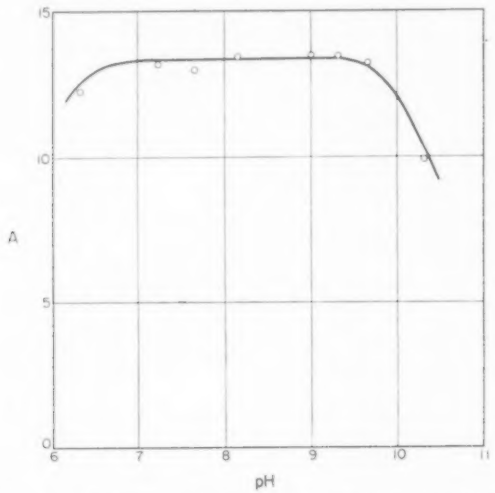

Fig. 1.—Influence of pH on the amount of extracted zinc-dithizonate (^{65}Zn labelled) in CCl_4. Activity, *A*, is expressed in 10^3 cpm.

aqueous phase was ten times larger than the volume of the organic phase, so that zinc was present in excess with respect to dithizone. Under these conditions, at pH 7·0 to 9·5 the maximum amount of zinc is extracted, which is in agreement with the predicted value.[1] In this region the influence of pH on the extraction of zinc is negligible.

By studying the influence of the time of shaking on the extraction of zinc it was found that in the pH region 7·0 to 9·5 equilibrium had already been attained after shaking for 10 min.

From Table I it is seen that by the proposed method it is possible to determine amounts of zinc of the order of 3×10^{-6} to 3×10^{-8} g/ml with an average precision of $\pm 1\%$. In the region of 3×10^{-9} g of zinc/ml the precision was substantially lower ($\pm 15\%$). The increase of the mean deviation of the arithmetic mean of a number of measurements,

$$\delta = \pm\sqrt{\frac{\Sigma\Delta^2}{n(n-1)}},$$

with a decreasing concentration of determined zinc is caused in part by a decrease of the measured activity, and in part by the fact that the elution of zinc from the material of the vessels employed influenced more and more the precision of the analysis. This is also to be seen from the fact that the amount of zinc found at the lowest concentrations was a little higher than the amount of zinc added. The substantial increase of the error in the analysis of the smallest amounts of zinc was caused above all by the fact

that the low specific activity of the employed radio-zinc necessitated, at this concentration, dilution with the analysed solution of non-active zinc in a ratio of 5:1. The variation of the measured activity at low count rates of 1800 cpm and high background of 600 cpm already greatly influenced the result of the analysis.

The presence of metals having a value of K lower than the K value of zinc dithizonate interferes in the determination of zinc.[1] To eliminate the influence of these cations various methods were examined. Firstly, the precipitation of interfering metals with hydrogen sulphide in an acidic medium was tried. This method was not successful, because the precipitate of sulphides formed contained nearly all of the zinc. The elimination of interfering elements by electrolysis was also unsuitable. In using thiosulphate as a masking agent, excess cadmium, cobalt and nickel interfered. The influence of interfering ions is best eliminated with diethanoldithiocarbamate. This reagent was chosen on the basis of the work of Margerum and Santacana[3] and proved successful. Diethanoldithiocarbamate forms crystalline precipitates with interfering metals, which do not adsorb traces of zinc on their surface, so that it is possible to add the reagent directly to the extracted solution. From Table I it is evident that in the determination of zinc in the presence of diethanoldithiocarbamate there is no interference even from a multifold excess of metals capable of extraction by dithizone: mercury, silver, platinum^{IV}, copper, bismuth, cadmium, cobalt, nickel, iron, lead and tin.

The proposed method is very simple and rapid. A single extraction of zinc from a solution containing an excess of interfering metals is far simpler than the conventional colorimetric determination of zinc by dithizone. From a comparison of our results with data from the literature[5] it is evident that determination of zinc by this method is far more sensitive than determination by activation analysis, spectral analysis, amperometry or flame photometry and more sensitive than colorimetric determination of zinc. This sensitivity could be further increased by the use of radio-zinc of higher specific activity. The method of isotopic dilution has the further advantage, that after the isotopes have been mixed there may be further losses of the element determined, in subsequent operations (for instance in separating the solution from the suspension in the analysis of samples), without endangering the result of the analysis.

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Zusammenfassung—Zink wurde bestimmt in Mengen von 10^{-6}–10^{-8} gZn/ml unter Anwendung einer einzigen Extraktion des Dithizonkomplexes. Die Genauigkeit beträgt 0,1%. Selbst 10^{-9} g Zn/ml können bestimmt werden, doch ist die Genauigkeit nur mehr 15%. In der Analyse stören selbst grosse Mengen von Metallen nicht, die ebenfalls Dithizonkomplexe bilden. Die Methode ist einfach und schnell, efordert eine einzige Extraktion und Zählung der Radioaktivität im Extrakt und ist genauer als die kolorimetrische Bestimmung mit dem selben Reagens.

Résumé—Le zinc a été dosé par simple extraction sous forms d'un complexe avec la dithizone: des quantités de 10^{-6} à 10^{-8} g de Zn/ml avec une précision moyenne de $\pm 0{,}1\%$ et des quantités de 10^{-9} g de Zn/ml avec une précision moyenne de $\pm 15\%$. Même un grand excès de métaux qui forment des complexes extractibles par la dithizone ne gêne pas l'analyse. La méthode est très simple et rapide; elle consiste en une extraction simple de la solution à analyser et en une mesure de la radioactivité du corps extrait. La méthode est plus sensible et plus précise que le dosage colorimétrique du zinc par la dithizone.

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DETERMINATION OF TRACES OF TELLURIUM

BISMUTHIOL II AS A REAGENT FOR TELLURIUM

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Summary—A spectrophotometric study of the new tellurium bismuthiol II reaction has been made to ascertain its suitability for the determination of traces of tellurium. The reaction mechanism is discussed. The yellow tellurium compound which is developed at pH 2·0–2·2 is stable, and is quantitatively extracted by chloroform at pH > 5. Addition of ammonium sulphate increases the rate of extraction. Two procedures, using aqueous solution with an absorption maximum at 395mμ, or solvent extraction with an absorption maximum at 335 mμ, are proposed. The extraction procedure makes the method more selective and sensitive. Many common ions do not interfere when EDTA and citrate are used as masking agents. The interferences from mercury, iron, copper, and selenium are serious. Beryllium or selenium may be used as collecting agents in the presence of EDTA for separation of tellurium. Selenium may subsequently be removed by volatilisation with bromine and hydrobromic acid. The absorptivity and sensitivity of the reaction were found to be 28,000 and 0·005 μg tellurium per cm^2, respectively, at 335 mμ.

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INTRODUCTION

BISMUTHIOL II (5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione) has been used for the determination of bismuth, palladium, and other metals.[5,9,10,12] This reagent has not been used for the determination of selenium or tellurium.* It was found that it reacts with selenium or tellurium below pH 5 forming a yellow coloration or precipitate which can be extracted by chloroform. A very sensitive and highly selective method for selenium is already available,[3] and therefore no attempt was made to utilise this reagent for selenium. However, a sensitive, selective, and satisfactory method for tellurium is still lacking; hence, an investigation aimed at utilisation of this reagent for determining traces of tellurium was undertaken.

Two sensitive methods for tellurium are available: (*a*) the iodide method of Johnson and Kwan[6] and (*b*) the dithiocarbamate method of Bode.[1,8] In the first method, the complex cannot be extracted by organic solvents and is subject to many interferences; in the second method the complex can be extracted by organic solvents and is more selective than other known methods for tellurium. But both methods are very sensitive to light, especially ultraviolet light. This is a serious drawback, since their absorption maxima are in the ultraviolet or near ultraviolet region. Not only is the colour reaction of the bismuthiol II method sensitive for traces of tellurium, but also the colour is stable. The variables for development and extraction of the coloured product have been studied. The precision of the method was found to be within $\pm 2\%$.

QUALITATIVE TEST

Bismuthiol II reacts with many metals forming coloured products in acidic or alkaline medium.[5,9,10,12] The selectivity due to the masking action of EDTA at various pH values has been reported.[4] Iron, copper, palladium, silver, gold, cadmium, mercury,

* After this paper was presented for publication, a paper appeared on the photometric determination of tellurium with bismuthiol II, J. Jankovský and O. Kšir, *Talanta*, 1960, **5**, 238.

thallium, lead, arsenic, antimony, bismuth, selenium, and tellurium still react with bismuthiol II in the presence of EDTA (ethylenediaminetetraacetic acid) and tartrate or citrate, but none of these, except silver, mercury, gold, and thallium, react at pH > 6. When cyanide is also added as a masking agent, at pH above 6, the reaction for thallium is highly selective. All platinum metals react with the reagent in the presence of EDTA, but above pH 10, only rhodium and iridium react in the presence of EDTA. At pH 2·2, cyanide does not effectively mask copper. Cerium^{IV} gives a white precipitate with bismuthiol II in the presence of EDTA at pH $< 2{\cdot}5$, probably due to oxidation.

PROPERTIES OF THE REAGENT AND ITS TELLURIUM COMPOUND

Bismuthiol II in the form of the acid or its potassium salt is pure white, changing to yellow when exposed to air. The potassium salt is soluble in water and stable, and its 1 % aqueous solution is almost colourless. Its solubility in organic solvents depends on pH, as the acid form is in general more soluble in the organic solvent.

With tellurium or selenium it forms an intense yellow-coloured compound or precipitate in acidic medium below pH 5, but the compound is decomposed above pH 8. The compound is extracted at pH 5–8 by alchohols, ketones, chloroform or carbon tetrachloride. The compound is stable in both aqueous solution and organic solvents. The reagent is oxidised, probably to disulphide, by many strong oxidising agents such as persulphate, ferricyanide, *etc.* The reaction with tellurium or selenium goes to completion relatively slowly.

The tellurium or selenium bismuthiol II precipitate is sensitive to high temperature; it changes from yellow to brick red at a temperature above 50°. It can be dried at room temperature under vacuum to a constant weight. Addition of methanol, ethanol, or acetone to the freshly prepared precipitate liberates elemental tellurium (see Table I). Bismuthiol I (2,5-dimercapto-1,3,4-thiodiazole) reacts in a similar

TABLE I.—REACTION OF ORGANIC SOLVENTS

Bismuthiol II precipitate	pH	Methanol	Ethanol	Acetone
Se	2·2	—	—	*
	6·8	—	**	**
Te	2·2	—	—	+
	6·8	+	+	+

— No apparent effect.
\+ Elemental tellurium separated, and the solution became dark.
* The precipitate dissolved to give a light yellow solution.
** Elemental selenium separated, and the solution showed a tan to reddish turbidity.

manner with selenium, tellurium, iron^{III}, copper, and other elements. However, when the yellow precipitate of tellurium (or selenium) bismuthiol I is dissolved by addition of ammonium hydroxide, elemental tellurium (or selenium) is precipitated. With bismuthiol II, the yellow selenium precipitate is more difficultly dissolved than the yellow tellurium precipitate. Upon addition of ammonium hydroxide, furthermore, neither elemental selenium nor elemental tellurium is immediately precipitated. This reduction reaction differentiates bismuthiol I from bismuthiol II.

EXPERIMENTAL

Reagents and Apparatus

Bismuthiol II (potassium salt of 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione): 1% aqueous solution.

Citric acid: 1*M*.

Ammonium sulphate: 50% w/v aqueous solution, adjusted to pH 2·2 with sulphuric acid.

EDTA (sodium salt of ethylenediaminetetra-acetic acid): 0·1*M*.

Standard tellurium solution: Dissolve 0·1 g of pure tellurium in 5 ml of concentrated sulphuric acid by heating. Fume to drive off most of the acid. After cooling, carefully add 100 ml of water and dissolve the tellurous acid precipitate by adding a minimum amount of 4*M* potassium hydroxide solution, then making to 1 litre. This solution contains 0·1 mg of tellurium per ml. More dilute solutions may be prepared by appropriate dilution from the stock solution.

Polyvinyl alcohol: 2% aqueous solution.

Other reagents are analytical reagent grade.

Beckman spectrophotometer Model DU and *Beckman pH meter Model G* or equivalent.

Procedure

Preparation of calibration curves

(*a*) *Aqueous Solution.* Transfer 0, 1·0, 2·0, 3·0, 4·0, and 5·0 ml of standard tellurium solution (25 μg of tellurium per ml) to 125-ml beakers. Add 1 ml of 1*M* citric acid and 1 ml of 2% polyvinyl alcohol solution, dilute with water to approximately 15 ml, add 2 ml of bismuthiol II solution, and set aside for 20–30 min. Adjust the pH to 6·5 carefully with 6*M* ammonium hydroxide, while stirring. Transfer to 25-ml volumetric flasks and make to volume. While stirring or mixing avoid the formation of foams. Measure the absorbance at 395 mμ using a reagent blank.

(*b*) *Solvent Extraction.* Transfer 0, 1·0, 2·0, 3·0, 4·0, and 5·0 ml of the standard tellurium solution (10 μg tellurium per ml) to 125-ml beakers, add 6 ml of ammonium sulphate solution, and dilute to approximately 25 ml. Add 1 ml of 1*M* citric acid solution, 3 ml of 1% bismuthiol II solution, and set aside for 20–30 min. Adjust the pH to 6·5 with 6*M* ammonium hydroxide. Transfer to 125-ml separatory funnels. Shake vigorously with 10·0 ml of chloroform for 1 min. After filtering through glass wool, measure the absorbance at 335 mμ, using a reagent blank.

The conditions, the volume of the solution, the pH, *etc.* should be carefully controlled in order to obtain good reproducibility.

DISCUSSION AND RESULTS

Spectral characteristics

The absorbance curves for the bismuthiol II and the tellurium compound in aqueous solution and in chloroform are shown in Figs. 1 and 2. The curves indicate

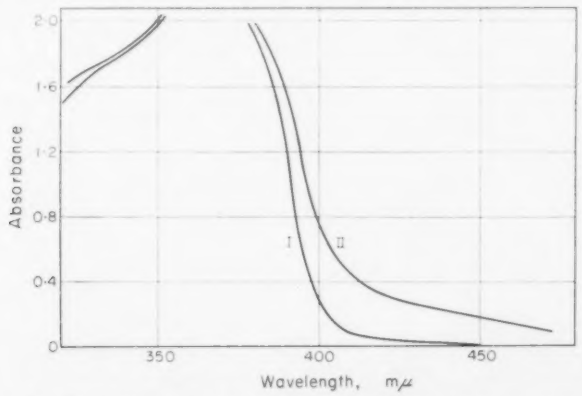

FIG. 1.—Absorption spectra, aqueous solution. (pH = 6·2: water as blank.)
I—Bismuthiol II.
II—40 μg Te + bismuthiol II in 10 ml of aqueous solution.

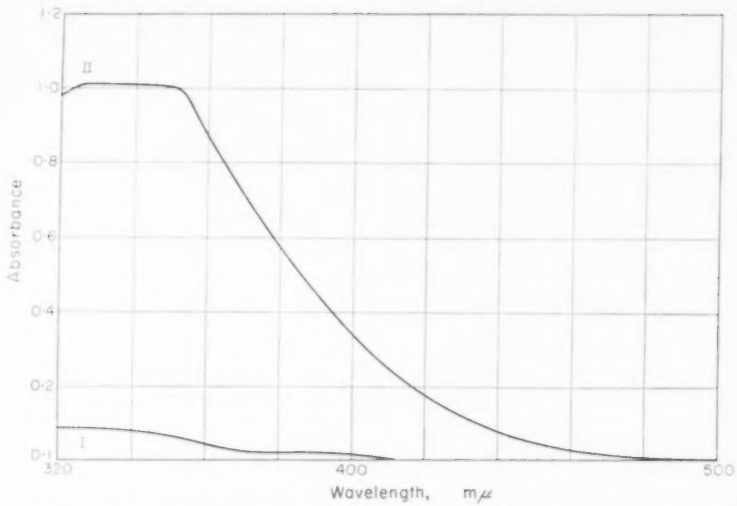

FIG. 2.—Absorption spectra, chloroform solution. (pH = 6·2 for extraction; chloroform as blank.)
I—Bismuthiol II in chloroform.
II—40 μg Te + bismuthiol II in 10 ml of chloroform.

that the tellurium compound in aqueous solution has an absorption maximum at 395–400 mμ, and in chloroform has an absorption maximum at 335–340 mμ. Since a small amount of bismuthiol II is also extracted by chloroform, a reagent blank should always be used when the chloroform extract is measured below 400 mμ.

Effect of reagents

It was found satisfactory to use 2 ml of 0·1% bismuthiol II solution in aqueous solution and 3 ml in the solvent extraction procedure (Fig. 3). When EDTA is added for masking purposes, the actual amount of EDTA required depends upon the amounts of interfering metals present. The amount of EDTA has no effect on the

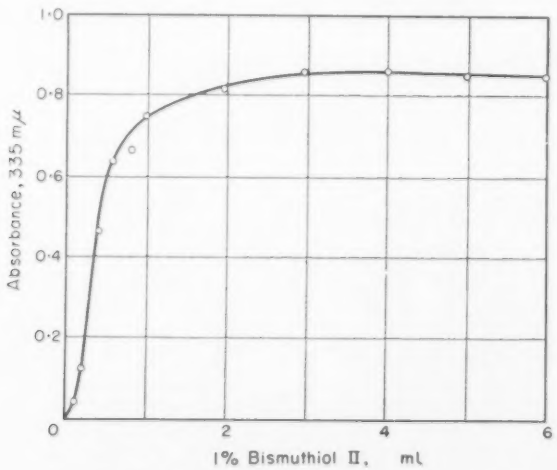

FIG. 3.—Effect of amount of bismuthiol II.

development of the tellurium colour. If EDTA is used to prevent the formation of insoluble hydroxides, it may be added after the tellurium colour has been developed at pH 2·2, and before the pH is adjusted to 6·5.

Effect of pH

The colour of the tellurium-bismuthiol II compound is developed only in acidic medium. If the solution is too acid, the bismuthiol II is precipitated in its acid form; if the pH of the solution is above 2·5, the formation of the tellurium-bismuthiol II compound is inhibited. It seems that the optimum pH for the colour development is at 2·0–2·3 (Fig. 4). Citric acid not only serves as a good buffer but also as a complexing

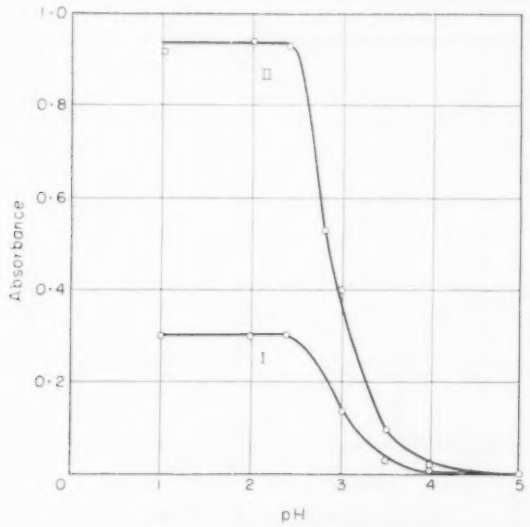

FIG. 4.—Effect of pH on colour development. I, 305 mμ: II, 340 mμ.

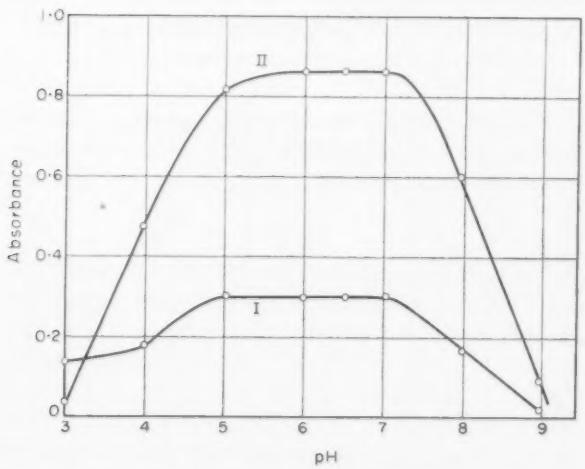

FIG. 5.--Effect of pH on solvent extraction. I, 395 mμ: II, 335 mμ.

agent to prevent hydrolysis of many metals. The amount of citric acid present has no effect. Tartaric acid may be used instead of citric acid. Fig. 5 shows that the coloured product is stable in neutral or slightly acid medium and that it decomposes in alkaline medium. For solvent extraction, the pH should be adjusted to 5–7. An optimum pH of 6·5 is chosen, because at this pH the amount of free bismuthiol II extracted is a minimum, and EDTA can mask the metals more effectively than in a more acidic medium.

Time required for colour development

The curve in Fig. 6 shows that the formation of the extractable reaction product required at least 20 min in order to obtain constant absorbance. It is believed that

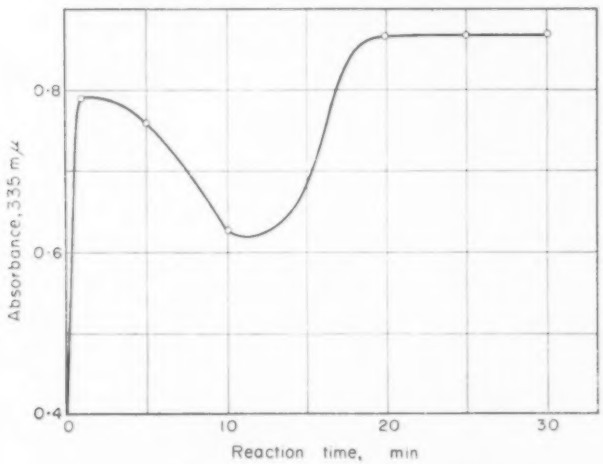

FIG. 6.—Effect of time on reaction.

the reaction of tellurium with bismuthiol II is a slow process which is similar to that of selenium with diaminobenzidine at pH 2–3. In the reaction of tellurium and bismuthiol II, some unextractable intermediate products may be formed in less than 20 min.

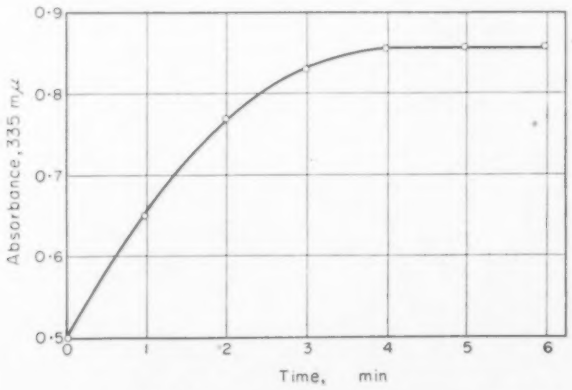

FIG. 7.—Effect of time on solvent extraction, no $(NH_4)_2SO_4$.

Effect of time of shaking

Fig. 7 shows that a minimum of 4 min of extraction time was required to obtain maximum extraction in the absence of sulphate. It was later found that the rate of extraction can be increased by addition of large amounts of sulphate. Extraction for 1 min with 3 g of ammonium sulphate gave slightly better extraction than extraction for 5 min without ammonium sulphate. Neither ammonium nitrate nor magnesium sulphate was as effective as ammonium sulphate in acting as a salting-out agent.

Beer's law and sensitivity

As indicated in Fig. 8, Beer's law is followed for both calibration curves in the range 5–50 μg of tellurium in 10 ml. It was also found that from 5–100 μg of

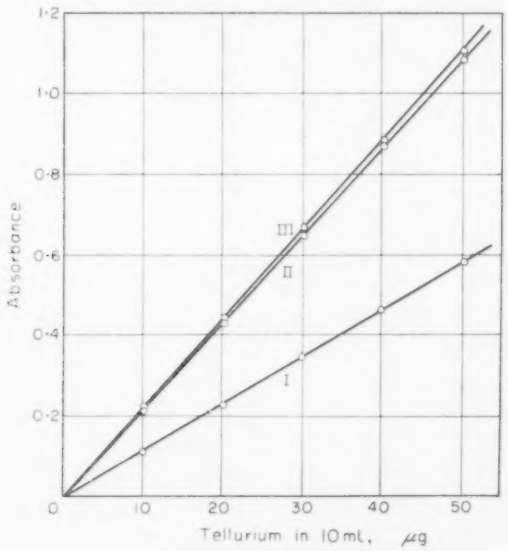

FIG. 8.—Calibration curves.
I—aqueous solution 395 mμ.
II—chloroform extract, 335 mμ, 5 min, no $(NH_4)_2SO_4$.
III—chloroform extract, 335 mμ, 1 min, 3 g $(NH_4)_2SO_4$.

tellurium in 10 ml of aqueous solution also followed Beer's law. The absorptivity was found to be 28,000 at 335 mμ and 14,700 at 395 mμ. The sensitivity was found to be 0.0005 μg of tellurium per cm^2 at 335 mμ and 0·009 μg of tellurium per cm^2 at 395 mμ.

Stability

The coloured product in chloroform was found to be stable for at least 24 hr. For the aqueous solution procedure, polyvinyl alcohol was used for preventing the formation of a precipitate. No appreciable turbidity was found after 1 hr. Turbidity may occur, however, after several hours.

Solvent extraction

Of the common solvents tried, chloroform and carbon tetrachloride were most satisfactory for extracting the coloured product of the reaction between tellurium and

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bismuthiol II (Table II). Isoamyl alcohol or hexanol extracted the yellowish compound, but the extract was turbid, and it was difficult to remove the white colloidal

TABLE II.—DIFFERENT SOLVENTS

20 μg Te in 10 ml

	Absorbance, 335 mμ	Remark
Chloroform	0·430	Clear
Carbon Tetrachloride	0·430	Clear
Isoamyl Alcohol	0·005	Turbid
n-Hexanol	0·005	Turbid
4-Methyl-2-pentanone	0·050	Yellow and turbid, including the reagent blank.

Addition of large amounts of salt such as ammonium chloride or potassium sulphate helped the extraction by isoamyl alcohol, n-hexanol, and 4-methyl-2-pentanone.

particles in the extract by filtration or centrifugation. The chloroform extract was clear. It was probable that the alcohol reacted with bismuthiol II to liberate colloidal sulphur.

From Fig. 5 it can be concluded that the extraction must be carried out at pH 5–7. A similar explanation to that in the case of the extraction of piazselenol may be proposed. The reaction between tellurium and bismuthiol II in acidic medium may be written as indicated in Fig. 9.

The dissociation constant, k, for equation (1) is 6×10^{-9}.[7] The concentration of Te^{4+} ion is small at pH 2, but the tellurium bismuthiol II compound is a very stable one. In the presence of bismuthiol II the reaction in equation (1) moves from left to right. It would be expected in such a case that complete reaction needs a large excess of bismuthiol II and a long time for development. As shown in equation (2), the charged complex of tellurium and bismuthiol II is formed in acidic medium and its extractability depends upon the number of charges. The uncharged complex shown in equation (3), formed at pH $>$ 5, is easily extracted by chloroform. At pH $>$ 3, the acidity is not strong enough for the reaction in equation (1) to proceed from left to right, and therefore no Te^{4+} ion is available for formation of the complex of tellurium bismuthiol II. This explains that at first a pH of approximately 2 is required to ensure the reaction of free tellurium ion with bismuthiol II; once the tellurium bismuthiol II complex has been formed, it can be extracted by adjusting to pH 6–7 in order to neutralise the positive charges of the complex. In alkaline medium, the tellurium bismuthiol II complex may gradually decompose in favour of the formation of tellurite.

Selectivity

Bismuthiol II reacts with many metals. Some of them may be masked by EDTA and citrate, which also prevents the hydrolysis of heavy metals. The interferences of $iron^{III}$ and copper are serious and cannot be masked by EDTA. Besides, strong oxidising agents react with bismuthiol II in a manner similar to tellurium. Large amounts of $arsenic^{III}$ give a white precipitate with the reagent and interfere at 335 mμ. Since many methods are available for separating tellurium from other elements,

$$H_2TeO_3 + 4H^+ = Te^{4+} + 3H_2O \qquad (1)$$

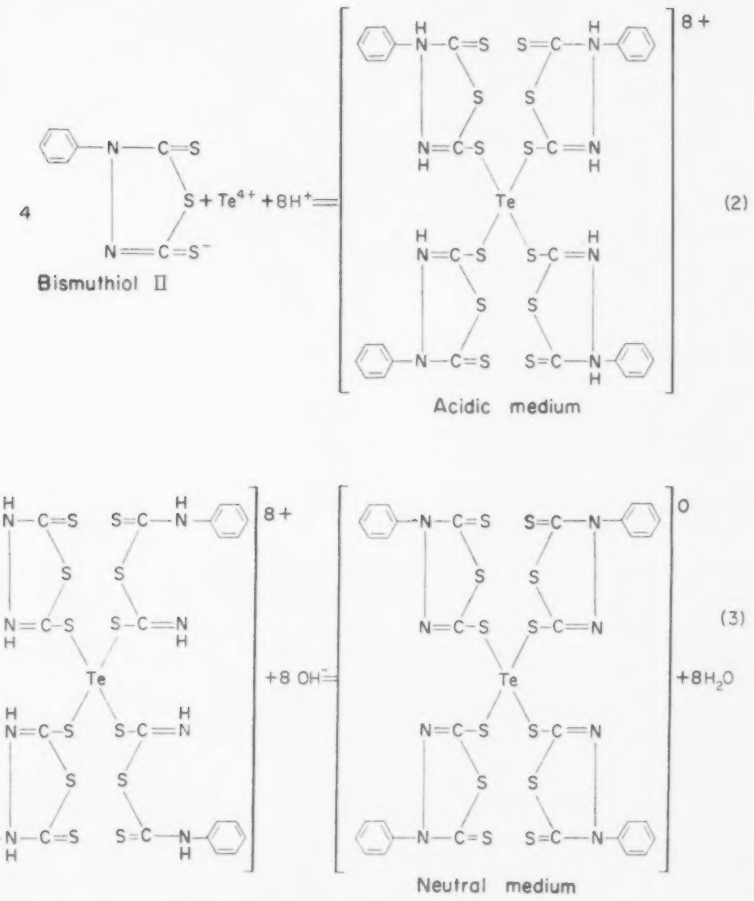

FIG. 9.

especially from selenium, it is better to separate tellurium from the others by co-precipitation with selenium in the elemental form. Selenium may be separated by bromine-hydrobromic acid evaporation or by diaminobenzidine. Many separation methods have been reviewed by Johnson.[2]

Interference studies

The metals interfering with this method have been described previously. Traces of iron and copper interfere. EDTA could not completely eliminate their interferences, since they still react with bismuthiol II at pH 2·2 in the presence of EDTA. Although they do not react with this reagent at pH > 6, the bismuthiol II complexes of iron and copper are not easily decomposed by EDTA at pH 6. Cyanide failed to mask copper at pH 2·2 but is effective at pH 6·5. Large amounts of arsenic^{III} give a white precipitate with the reagent at pH 2·2, and interfere at 335 mμ. Selenium reacts similarly to

tellurium and must be removed before determination. Reaction of bismuth or cadmium with the reagent was not completely masked by EDTA at pH 2·2 but their bismuthiol II complexes were easily decomposed by EDTA at pH 6·5. Therefore small amounts of bismuth or cadmium can be tolerated. The results of determining tellurium in the presence of foreign ions are shown in Table III. In general, it is

TABLE III.—DETERMINATION OF TELLURIUM IN PRESENCE OF FOREIGN IONS
TELLURIUM TAKEN: 20·0 μg

Foreign ion	Amount added	Tellurium found, μg
Be^{2+}	0·05 m mole	20·0
Nb^{5+}	0·001 m mole	20·2
Al^{3+}	0·01 m mole	19·5
In^{3+}	1 mg	20·0
Ga^{3+}	0·1 mg	20·1
Bi^{3+}	0·1 mg	20·2
Fe^{3+}	13 μg	24·0
Cu^{2+}	10 μg	20·7
As^{3+}	47 μg	20·4
Cd^{2+}	1 mg	20·0

recommended that tellurium be separated from other interfering elements before employing bismuthiol II. Ferric hydroxide and aluminium hydroxide have been used as collecting agents for separating tellurium in its elemental form. Since beryllium does not react with bismuthiol II and EDTA, it would be advantageous to use beryllium hydroxide as a collecting agent in the presence of EDTA. If selenium is also present, both selenium and tellurium are separated along with beryllium hydroxide. The precipitates are then treated with bromine and hydrobromic acid to remove selenium. The bismuthiol II method is then followed. An attempt was made to separate tellurium from iron by a Dowex 50 cation-exchanger (hydrogen form); it was found that both iron and tellurium were absorbed by the resin. Chloride, bromide, sulphate, nitrate, and phosphate do not interfere.

Determination of tellurium in selenium

It would be interesting to determine traces of tellurium in selenium because not only selenium in general interferes with the methods for tellurium but also it is a good co-precipitating agent for separating traces of tellurium. For employing the proposed method, selenium must be removed before determination of tellurium. Bromine and hydrobromic acid have been used for removing selenium.[11] A study was made to test the feasibility of the bromine-hydrobromic acid method to remove large amounts of selenium in the determination of traces of tellurium.

Synthetic mixtures containing 1–2 mg of selenium and 0–40 μg of tellurium were prepared. To the mixture (5 ml) in a 100-ml beaker was added 0·5 ml of redistilled hydrobromic acid. Some bromine vapour was introduced. The mixture was evaporated on a hot plate at 100° or in a water bath. After drying, the operation was repeated three times by the addition of 1 ml of hydrobromic acid (rinsing down the side of the beaker) and the introduction of bromine vapour. Finally, the residue was baked at 100° for 10 min in order to expel any traces of bromine and hydrobromic acid, which also react with bismuthiol II. The beaker was cooled, 1 ml of 1*M* citric acid, 6 ml of ammonium sulphate solution, 20 ml of water, and 3 ml of 1% bismuthiol II solution were added. The solution was set aside for 20–30 min, and then extracted with 10 ml of chloroform, after adjusting the pH to 6·5. The results shown in Table III are excellent.

If high sensitivity is not required, after removing selenium the tellurium may simply be determined in aqueous solution instead of using solvent extraction. The excellent recovery of traces of tellurium suggests that selenium can be used to collect traces of this element and thus separate it from others. No loss of tellurium was noticed during volatilisation of selenium with bromine–hydrobromic acid.

TABLE IV.—DETERMINATION OF TELLURIUM IN MIXTURES OF SELENIUM-TELLURIUM AFTER VOLATILISATION OF SELENIUM AS BROMIDE

Tellurium present, μg	Tellurium found, μg	
	1 mg Se added*	2 mg Se added†
none	0	0
20·0	20·0	20·0
30·0	29·8	29·5
40·0	40·0	39·8

* Chloroform extraction procedure.
† Aqueous solution procedure.
For 30·0 μg of tellurium without addition of selenium, recovery of 30·0 μg of tellurium was obtained in both aqueous and chloroform procedures.

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Composition of compound

The Job's curves shown in Fig. 10 obtained in aqueous solution at 395 mμ indicate that a complex of 1 tellurium:4 bismuthiol II was formed. It was thought that the

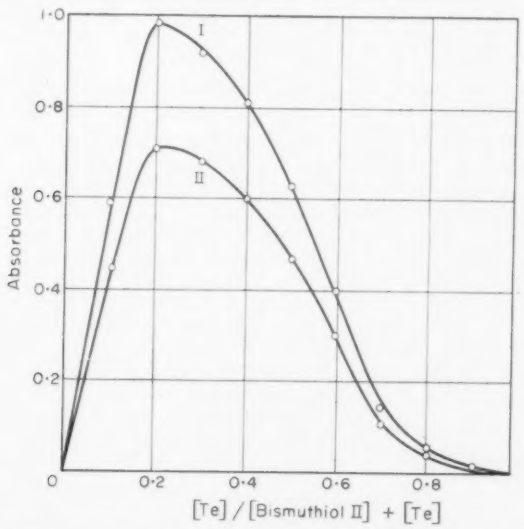

FIG. 10.—Job's curves (total concentration = $3{\cdot}2 \times 10^{-4}$ M. I, 400 mμ: II, 420 mμ.)

reaction between tellurium and bismuthiol II might be a redox reaction. In order to confirm the presence of tellurium, the precipitate was dissolved in a dilute potassium hydroxide solution using heat. The solution was adjusted to pH 8 with hydrochloric acid and sodium carbonate. Small amounts of EDTA and cyanide were added, followed by 1 ml of 1% sodium diethyldithiocarbamate solution. The chloroform

extract was decomposed with a mixture of nitric acid and perchloric acid and then tested with diethyldithiocarbamate in the presence of EDTA and cyanide. Tellurium was found in both the precipitate and the chloroform extract. It is known that the palladium bismuthiol II complex has a 1 : 2 composition[10] and the bismuth bismuthiol II complex has a 1 : 3 composition.[12] The tellurium bismuthiol II complex would be expected to have a composition of 1 : 4. Based on the presence of tellurium in the reaction product, the Job's curves, and the fact that tellurium has less tendency to be co-ordinated, the tellurium bismuthiol II complex may be presumed to be a salt, with the structure shown above. The Job's curves also show that complexes with other compositions may also be formed when tellurium is in excess.

Zusammenfassung—Ein spectrophotometrische Studie der Reaktion zwischen Tellur und Bismuthiol II wurde angestellt um die Brauchbarkeit der Reaktion zur Bestimmung von Tellur sicherzustellen. Der Reaktionsmachanismus wird diskutiert. Die gelbe Verbindung entsteht bei pH 2–2·2, ist stabil und wird durch Chloroform bei pH kleiner als 5 quantitativ extrahiert. Zwei Methoden werden vorgeschlagen. Eine arbeitet mit wässriger Lösung bei einem Absorptionsmaximum bei 395 mμ, die zweite nach Solventextraktion bei 335 mμ. Die zweite Methode ist selektiver und empfindlicher. Zahlreiche der gewöhnlichen Metallionen stören nicht, wenn ÄDTE und Zitrat als Maskierungsmittel anwesend sind. Störungen durch Quecksilber, Eisen, Kupfer und Selen sind schwer. Beryllium und Selen können als Sammler verwendet werden um Tellur abzutrennen, wenn ÄDTE gegenwärtig ist. Selen ist anschliessend durch Behandlung mit Brom und Bromwasserstoffsäure zu verflüchtigen. Der Absorptionskoeffizient ist 28,000 bei 335 mμ und die Empfindlichkeit bei derselben Wellenlänge ist 0.005 μg Tellur per cm².

Résumé—Les auteurs ont fait une étude spectrophotométrique de la nouvelle réaction tellure-bismuthiol II pour le dosage de traces de tellure. Le mécanisme de la réaction est disucté. Le composé jaune du tellure formé à pH 2,0–2,2 est stable et extrait quantitativement par le chloroforme à un pH supérieur à 5. L'addition de sulfate d'ammonium augmente la vitesse de l'extraction. Deux modes opératoires sont proposés: en solution aqueuse avec un maximum d'absorption à 395 mμ ou extraction par un solvant avec un maximum d'absorption à 335 mμ. La technique par extraction rend la méthode plus sélective et plus sensible. De nombreux ions courants ne gênent pas quand on utilise l'EDTA et le citrate comme agents complexants. Le mercure, le fer, le cuivre et le sélénium gênent sérieusement. Le béryllium ou le sélénium peuvent être utilisés comme agent collecteur en présence d'EDTA pour la séparation du tellure. Le sélénium peut être séparé par volatilisation avec du brome et de l'acide bromhydrique. Les valeurs respectives suivantes ont été trouvées pour l'absorption et la sensibilité de la réaction: 28.000 et 0,005 μg de tellure par cm² à 335 mμ.

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EINE NEUE POLARIMETRISCHE METHODE ZUR BESTIMMUNG VON OPTISCH INAKTIVEN IONEN—I

BESTIMMUNG DES QUECKSILBERS

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Zusammenfassung—Es wird eine neue allgemein anwendbare Methode zur polarimetrischen Bestimmung von optisch inaktiven substanzen beschrieben. Zu diesem Zweck wird das betreffende Ion (im Falle einiger Kationen nach vorherigem Anionisieren) mit Hilfe eines optisch aktiven Reagenz gefällt oder in eine Komplexverbindung übergeführt. Das Reaktionsprodukt wird isoliert, gelöst und polarimetriert. Als Beispiel wird die Bestimmung des Quecksilbers erläutert. Das Hg^{2+}-Ion wird mit Hilfe von Kaliumjodid in Tetrajodomerkuriat übergeführt und dann mit einer Chininmonochlorhydratlösung gefällt. Der filtrierte und gut gewaschene Niederschlag wird in Aceton gelöst und die so erhaltene Lösung bei Zimmertemperatur polarimetriert.

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IM folgenden wird eine neue polarimetrische Methode zur Bestimmung optisch inaktiver Ionen beschrieben.

Dieser Methode können folgende allgemeine Reaktionen zugrunde liegen:

$$A + R_a = C_a \quad (1)$$

$$A + R_i = C_i \quad (2)$$

$$C_i + R_a' = D_a \quad (2')$$

A = ein zu analysierender Stoff; R_a = ein optisch aktives Reagens (Kation, Anion oder ein Komplex–bzw. Chelatbildner); C_a = eine leicht oder schwerlösliche optisch aktive Verbindung: Salz oder Komplex; R_i = ein optisch inaktives einfaches Anion oder eines, das Chelate zu bilden fähig ist; C_i = ein optisch inaktives Anion oder Kation; R_a' = ein optisch aktives Kation oder Anion; D_a = eine schwerlösliche, optisch aktive Verbindung.

Falls ein Niederschlag entsteht (D_a u. C_a), wird dieser abfiltriert, vom R_a- oder R_a'-Überschuss durch Waschen befreit, gelöst, in einen Messkolben gebracht und polarimetriert. Der Niederschlag kann auch durch Extraktion abgetrennt werden, selbstverständlich unter der Voraussetzung, dass nicht auch ein Teil des optisch aktiven Reagensüberschusses (R_a bzw. R_a') extrahiert wird.

Falls eine lösliche optisch aktive Verbindung entsteht (Gleichung 1), wird diese durch Extraktion getrennt, in einen Messkolben gebracht und polarimetriert.

Das Lösungsmittel wird so gewählt, dass es keinerlei Einfluss auf das Drehungsvermögen der optisch aktiven Verbindung haben kann.

Die Methode ist allgemein anwendbar, ist leicht auszuführen und weist gegenüber der kolorimetrischen den Vorteil einer linearen Abhängigkeit des Drehungsvermögens von der Konzentration—wie sie ein Gesetz vom Typ Bouguer-Lambert-Beer fordert—in viel weiteren Grenzen auf.

Vor allem ist die Bestimmung von Anionen nach vorhergehender Fällung mit organischen optisch aktiven Basen sehr bequem.

Die Kationen werden zuerst in negative Säurekomplexe übergeführt und dann mit optisch aktiven organischen Basen gefällt.

Als Fällungskationen kann eine optisch aktive organische Base bzw. ihr Salz (Chinin, Codein, Morphin, Cinchonidin, Cinchonin, Conchinin, Nicotin, Thebain, Strychnin, ua.), oder ein optisch aktives Oniumsalz (Tetralkylammonium, Phosphonium, Arsonium, Sulfonium, usw.) benützt werden.

Anhand dieser Methode können nachstehende Ionen bestimmt werden: Heteropolysäuren; Bi^{3+}, Cd^{2+}, Hg^{2+} nach vorangehender Überführung in Iodokomplexe; Fe^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+} nach Überführung in Cyanokomplexe; Hg^{2+} in Form von $HgCl_2$ oder nach Überführung in Thiocyanatokomplexe; Au^{3+}, Pt^{4+} nach Überführung in Chlorokomplexe; UO_2^{2+} als Salicylatkomplex; MoO_4^{2-}, WO_4^{2-}, I^-, Br^-, CN^-, SCN^-, usw.

Die Genauigkeit und Empfindlichkeit der Methode kann auf nachstehende Weise erhöht werden:

(1) Fällung mit Stoffen von grossem molekularen Drehungsvermögen.

(2) Polarimetrieren im Spektralgebiet grösster molekularer Drehung des aktiven Stoffes. Es ist zweckmässig die Rotationsdispersion jedes zur Fällung benutzten Stoffes zu kennen.

(3) Benutzung eines objektiven Apparats, z.B. eines photoelektrischen Spektralpolarimeters.

(4) Heranziehen des Faraday' schen Effektes durch Kompensation der Drehung mit Hilfe eines magnetischen Feldes und Bestimmung der erforderlichen Stromstärke.

Zur Illustration dieser Arbeitsweise sei die Bestimmung des Quecksilbers beschrieben.

Die Methode beruht auf den Reaktionen (2) u. (2') und zwar führt man das Hg^{2+}-Ion zuerst mit Hilfe von Kaliumjodid in den Komplex $[HgJ_4]^{2-}$ über, der dann mit einem organischen optisch aktiven Kation (Chinin) bei Zimmertemperatur gefällt wird. Nach Abfiltrieren des Niederschlages und entfernen des Chininchlorhydrats durch gründliches Waschen, wird er in Aceton gelöst. Man polarimetriert dann die acetonische Lösung des Chinintetraiodomerkuriates.

ARBEITWEISE

Die 10–300 mg Hg enthaltende Lösung (höchstens 100 ml) des Merkurisalzes wird mit einer 2%igen wässerigen KJ-Lösung tropfenweise bis zum Lösen des HgJ_2-Niederschlages, versetzt. Das gebildete $[HgJ_4]^{2-}$-Anion wird dann mit einer 5%-igen Chininmonochlorhydratlösung im Überschuss bei Zimmertemperatur gefällt. Es bildet sich Chinintetrajodomerkuriat ($C_{20}H_{25}O_2N_2$) $[HgJ_4]$. ein weisser (in Säuren schwer löslicher) Niederschlag, den man abfiltriert und mit kaltem Wasser 5–6 mal wäscht.

Der vom Chininüberschuss befreite Niederschlag wird auf dem Filter in Aceton gelöst und die so erhaltene Lösung in einem Messkolben (100 ml) aufgefangen. Man wäscht das Filter gut mit Aceton und füllt den Kolben mit Wasser bis zum Marke auf. Die acetonisch Lösung des Chinintetrajodomerkuriats wird bei Zimmertemperatur polarimetriert.

Wir fanden, dass weder eine Temperaturerhöhung von 20° bis 50°, noch das Verhältnis Aceton: Wasser noch das Ansäuren der Lösung mit HCl, einen Einfluss auf den Rotationswinkel haben.

Es wurde mit einem Lippich-Halbschattenpolarimeter mit Na-Lampe gearbeitet, das eine Genauigkeit von 36″ (1°/100) erlaubte, die Rohrlänge betrug 20 cm.

Eine Bestimmung dauert nicht länger als 30 min.
Die Messergebnisse sind in Tabelle I und Figur 1 wiedergegeben.

TABELLE I
$\alpha_0 = 2°51'36''$

mg Hg/100 ml, y	α	$\alpha-\alpha_0$	$\alpha-\alpha_0$ im 1°/100, x
9·98	2°45′	6′36″	11
19·90	2°41′24″	10′12″	17
39·94	2°31′48″	19′48″	33
59·90	2°22′12″	29′24″	48
79·87	2°15′	36′36″	61
99·84	2° 6′36″	45′	75
139·77	1°48′	1° 3′36″	106
159·74	1°43′48″	1° 7′48″	113
179·71	1°34′12″	1°17′24″	129
199·68	1°22′12″	1°29′24″	149
299·52	0°45′	2° 6′36″	211

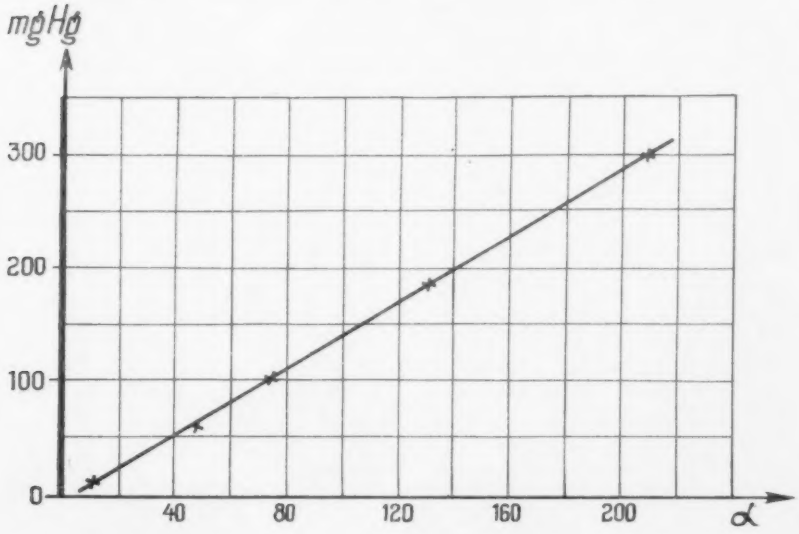

FIG. 1.

Nach Verarbeitung der Ergebnisse der 11 Bestimmungspaare mit Hilfe der Methode

der kleinsten Quadrate, wurden die Koeffizienten A_0 und A_1 der Gleichung $y = A_0 + A_1x$, die zur Berechung der Quecksilbermenge (in mg) dient, aus dem Rotationswinkel x (in 1/100° ausgedrückt) berechnet. Man erhält die für die obigen Arbeitsbedingungen gültige Funktion $y = -7{,}1 + 1{,}433x$ = mg Hg/100 ml.

Summary—A new general method for the determination of optically inactive substances is described. The ion to be determined, as such, or after anionisation (in the case of cations), is precipitated, or is converted into a complex by means of an optically active reagent. The reaction product is dissolved and the rotation is determined. For example, the ion Hg^{2+} is converted by means of potassium iodide into the tetra-iodomercurate, which is precipitated with a solution of quinine hydrochloride. The precipitate is filtered off, washed and dissolved in acetone; the rotation of the resulting solution is determined at room temperature.

Résumé—Une nouvelle méthode générale de dosage de substances optiquement inactives est basée sur la précipitation des anions (ou des cations après transformation en anions) par un agent complexant optiquement actif. Le produit de la réaction est dissous et le pouvoir rotatoire est déterminé. Les auteurs décrivent le dosage du mercure. L'ion mercurique est transformé au moyen d'iodure de potassium en anion tétra-iodo mercurate, qui est précipité par du chlorhydrate de quinine. Le précipité est filtré, lavé et dissous dans l'acétone, et le pouvoir rotatoire est déterminé à la température ambiante.

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SEPARATION AND DETERMINATION OF SCANDIUM USING *N*-BENZOYLPHENYLHYDROXYLAMINE*

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Summary—Scandium may be determined using *N*-benzoylphenylhydroxylamine, which precipitates a complex containing scandium and reagent in the ratio 1:3. This precipitate may be utilised for the gravimetric determination of scandium by conversion to Sc_2O_3 at 600°. It is possible to separate scandium from zirconium, titanium and the rare earth elements by extraction.

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THE analytical reactions of scandium have not been studied to any great extent.[1] For its separation from other elements and quantitative determination several inorganic precipitants have been recommended, *e.g.* hydrofluoric, fluorosilicic, pyrophosphoric, hypophosphorous acids, *etc.* Organic precipitants for scandium have been less studied. For the separation of scandium from other elements, ion-exchange chromatography and extraction with organic solvents have been used.

In the present work to select new reagents for scandium, the similarities with the quadrivalent elements zirconium, hafnium and thorium, brought about by the close values of the ionic radii of these elements, have been taken into account. As an analogue for cupferron, *N*-benzoylphenylhydroxylamine was used. This is a reagent for the determination of titanium, vanadium, molybdenum, niobium, tantalum and other elements. Our experiments showed that in a strongly acid medium *N*-benzoylphenylhydroxylamine precipitates zirconium quantitatively and, in a weakly acid medium, thorium and scandium. The conditions for the precipitation and extraction of the *N*-benzoylphenylhydroxylaminate of scandium and the composition of the precipitate were determined. Examples of the separation of scandium from zirconium and the rare earth metals are given here.

The *N*-benzoylphenylhydroxylamine reagent was synthesised by Shome's method[2] and the scandium chloride solution was prepared by dissolving spectrally pure scandium oxide in the minimum quantity of concentrated hydrochloric acid with continuous careful heating until the cloudiness disappeared. The solution obtained was evaporated almost to dryness, and the residue was dissolved in the necessary volume of water. The titre of the solution was determined by precipitation of the hydroxide with ammonia and weighing as Sc_2O_3. For complete precipitation of the scandium it is necessary to add a small excess of reagent and keep the pH $>5{\cdot}2$. The results of quantitative determinations of a pure scandium salt solution are shown in Table I.

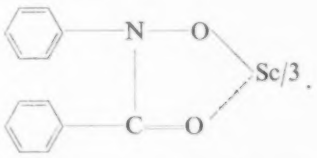
To study the composition of the scandium *N*-benzoylphenylhydroxylaminate the precipitate was filtered off in a sintered-glass filter-crucible, washed with 50 ml of hot water and 30–50 ml of ether, then dried to constant weight at 105°–110°. Part of the precipitate was then heated to constant weight at 800°–900°. The results showed

* Translated from the Russian, *Zavodskaya Lab.*, 1959, **12**, 1435.

TABLE I.—DETERMINATION OF SCANDIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

Sc_2O_3, *mg*	
Taken	Found
4·5	4·5; 4·6; 4·5; 4·5
2·7	2·7; 2·8; 2·7
3·6	3·7
1·8	1·8

that the chemical composition of the precipitate separating from a weakly acid solution corresponds with the formula



To find the stability of scandium N-benzoylphenylhydroxylaminate to heat we carried out a thermogravimetric analysis (Fig. 1). The precipitate was stable up to 220°.

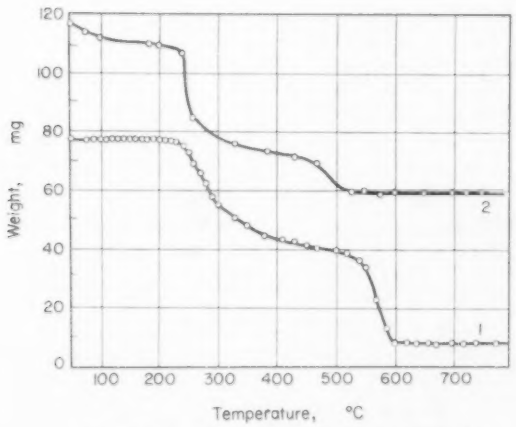


FIG. 1.—Results of thermogravimetric analysis.
1.—*N*-Benzoylphenylhydroxylaminate of scandium.
2.—Cupferrate of scandium.[4]

To obtain the form used for weighing (Sc_2O_3), the precipitate need only be heated to 600°.

Scandium may be separated from the rare earth elements as follows. To 100 ml of a solution containing scandium and rare earth elements 30 ml of a 20% solution of ammonium acetate were added and a few ml of acetic acid (1:1), so that after precipitation the solution pH should be about 5·4. After precipitation of the scandium, ammonium was added to the filtrate and the precipitate of rare earth hydroxide was filtered off through a fine filter, dried and heated to constant weight at 800°–900°. The results are shown in Table II.

TABLE II.—SEPARATION OF SCANDIUM FROM RARE EARTH ELEMENTS

Taken, *mg*		Found, *mg*	
Sc_2O_3	Σ Rare earths	Sc_2O_3	Σ Rare earths
4·5	4·9	4·6 and 4·5	4·9
4·5	29·7	4·6 and 4·7	29·6 and 29·5
2·7	29·7	2·6	29·7
1·8	79·2	1·8	79·3

Zirconium in a strongly acid medium (3*N* hydrochloric acid) is precipitated quantitatively by *N*-benzoylphenylhydroxylamine, while scandium is not precipitated under these conditions. The separation of scandium and zirconium can be carried out using this fact. For this purpose a titrated solution of zirconium oxychloride was used. Firstly the zirconium was precipitated in a 2*N* hydrochloric acid solution. The filtrate was evaporated to about 100 ml and the excess hydrochloric acid was neutralised with ammonia, using methyl orange as indicator. The precipitation and determination of the scandium was carried out subsequently (Table III).

Scandium *N*-benzoylphenylhydroxylaminate can be extracted with n-butyl alcohol, amyl acetate, benzene, chloroform and iso-amyl alcohol. To determine the conditions for extraction, a measured amount of scandium chloride solution from a

TABLE III.—SEPARATION OF SCANDIUM FROM ZIRCONIUM

Taken, mg		Found, mg	
Sc_2O_3	ZrO_2	Sc_2O_3	ZrO_2
2·7	3·2	2·6 and 2·7	3·3 and 3·2
4·5	16·0	4·6	16·0
3·6	16·0	3·6	16·0
1·8	48·0	2·0	47·8
2·7	48·0	2·9	47·9

pipette was introduced into a 30-ml separating funnel. This was diluted with distilled water to a given volume, then dilute hydrochloric acid or ammonia was added to give the required pH. An equal volume of reagent was then added, in iso-amyl alcohol. After shaking, the scandium which had passed into the organic solvent and that remaining in the aqueous phase were determined spectrophotometrically using the reaction with Alizarin Red-S. The effect of the organic substances was taken into account using the method of Eberle and Lerner.[3]

To determine the amount of scandium extracted by the organic solvent two extractions were carried out, with shaking, using 5 ml of 1–2*N* hydrochloric acid. The aqueous phase containing the scandium was introduced into a 100-ml volumetric flask. To this solution a few ml of distilled water were added and 2 ml of a 0·1% alizarin red-S solution, and the liquid was carefully neutralised with ammonia (1:3) until a red colour appeared. Then 5 ml of a 20% buffer solution of ammonium acetate (pH 3·5) were added, the solution was cooled to room temperature, and was diluted with water to an exact volume. The absorption was measured spectrophotometrically at 520 mμ in a 5-cm cell. The results obtained are shown in Figs. 2 and 3.

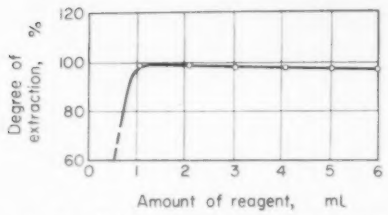


FIG. 2.—Extraction of the *N*-benzoylphenylhydroxylaminate of scandium with various amounts of reagent (0·5% solution of N-benzoylphenylhydroxylamine in iso-amyl alcohol).

The distribution equilibrium occurred quickly. Shaking for 4 min produced quantitative separation of the scandium. The presence of NH_4^+, Na^+, NO_3^- and Cl^- ions produced no noticeable effect on the degree of extraction.

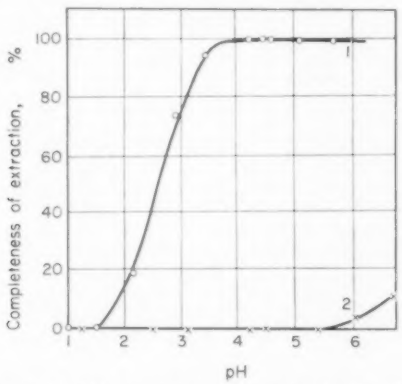


FIG. 3.—Extraction of the *N*-benzoylphenylhydroxylaminates of scandium and rare earth elements at various pH of the aqueous phase:
1.—Scandium extractions.
2.—Σ Rare earth elements extraction.

A study of the extraction of the rare earth elements showed that at pH <5·8 they are not extracted (see Fig. 3, curve 2). This fact was used for separating them from the scandium at pH ~4·5. Our experiments also showed that the *N*-benzoyl-

TABLE IV.—SEPARATION OF SCANDIUM FROM RARE EARTH ELEMENTS, ZIRCONIUM AND TITANIUM BY EXTRACTION

Taken, *mg*			Found, *mg*
Sc_2O_3	Oxides of other metals		
0·025	rare earth	10	0·027
0·025	rare earth	30	0·027
0·050	rare earth	10	0·050
0·050	rare earth	30	0·051
0·075	rare earth	10	0·074
0·075	rare earth	30	0·077
0·025	ZrO_2	4·8	0·026
0·050	ZrO_2	3·2	0·052
0·075	ZrO_2	3·2	0·075
0·025	TiO_2	1	0·026
0·050	TiO_2	1	0·053

phenylhydroxylaminates of zirconium and titanium are extracted quantitatively in a strongly acid medium, with iso-amyl alcohol (for zirconium 1–8*N* hydrochloric acid; for titanium 5–10*N* hydrochloric acid), while the scandium is not extracted. A method for the separation of scandium from zirconium and titanium can be based on this fact. To carry out this separation zirconium in 2*N* hydrochloric acid and titanium in 5*N* hydrochloric acid were extracted twice (5 ml) with a 3% solution of *N*-benzoylphenylhydroxylamine in iso-amyl alcohol. The results are shown in Table IV.

Zusammenfassung—Scandium kann mit n-Benzoylphenylhydroxylamin als ein Komplex gefällt werden, der Metall und Reagens im Verhältnis 1:3 enthält. Scandium wird gravimetrisch bestimmt; nach Verglühen zum Sesquioxyd bei 600°C. Die Trennung des Scandiums von Zirkon, Titan und seltenen Erden mittels Extraktionsmethoden ist möglich.

Résumé—Le scandium peut être précipité par la n-benzoylphénylhydroxylamine sous forme d'un complexe contenant scandium et réactif dans le rapport 1/3. Ce précipité peut être utilisé pour le dosage gravimétrique du scandium par transformation en SC_2O_3 à 600°. Il est possible de séparer le scandium du zirconium, du titane et des terres rares par extraction.

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ACTIVATION ANALYSIS OF MANGANESE IN CAST IRON AND HIGH-ALLOY STEELS

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Summary—A method for the determination of manganese in cast iron and high-alloy steels has been developed. Self-shielding errors and neutron flux irregularities were avoided by the use of an internal standard. Two procedures, integral counting and pulse height discrimination were used. The method was tested on standard samples. The results obtained on samples with a widely differing composition are in excellent agreement with those obtained by classical chemical analysis.

INTRODUCTION

ACTIVATION analysis with thermal neutrons is not only capable of high sensitivity for a large number of elements, but also allows accurate determinations as a non-destructive method of analysis. This was clearly demonstrated by several authors, among them Leliaert *et al.*,[1–3] who determined vanadium and tungsten in high alloy steels using an internal standard technique.[3]

In this paper an investigation of the direct determination of manganese in cast iron and high-alloy steels without chemical separation is described; iron or other long living species present in the high-alloy steels were used as internal standard.

As manganese has a quite large cross-section for thermal neutrons and a rather short half-life, high disintegration rates can be expected even after short irradiations at a moderate neutron flux.

Several authors have already determined manganese by activation analysis, namely Bowen[4] in biological material, Daudel[5] in aluminium alloys and Fisher *et al.*[6] in cobalt samples.

NUCLEAR DATA

Natural manganese occurs as the single isotope ^{55}Mn and gives rise to only one radioactive species, ^{56}Mn, a complex β-γ-emitter with 2·58 hr half-life, activation cross-section 13·4 barn. The decay scheme[7] is given in Fig. 1.

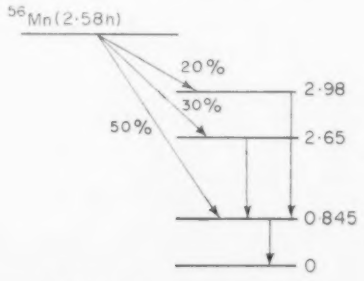

FIG. 1.—Decay scheme of ^{56}Mn.

Interfering activities arising from steel constituents

It is obvious that by thermal-neutron-activation of cast iron or high-alloy steels a large number of radioactive species can be formed, as appears from Table I.

TABLE I.—RADIOACTIVE SPECIES PRODUCED FROM CAST-IRON OR STEEL CONSTITUENTS

Element	% in steel	Natural isotope	$\theta \cdot \sigma_{act}$	Isotope produced	$T_{1/2}$	Radiation and energy
V	<2·5	^{51}V	4·5	^{52}V	3·75 m	β^- 2·7//γ 1·46
Cu	0·1	^{65}Cu	0·68	^{66}Cu	5·1 m	β^- 2·63/1·59//γ 0·191
Ti	up to 50	^{50}Ti	0·007	^{51}Ti	5·8 m	β^- 1·5/2·13//γ 0·3/0·6/0·9
Nb	0·30	^{93}Nb	1·4	^{94m}Nb	6·6 m	β^- 1·3//γ 0·04/0·9
Co	up to 45	^{59}Co	17	^{60m}Co	10·5 m	γ 0·058
Mo	seldom 2	^{100}Mo	0·019	^{101}Mo	14·6 m	β^- 2·2/1·2//γ 0·96/0·191
Mn	0·25–1·3	^{55}Mn	13	^{56}Mn	2·56 h	β^- 2·86/1·05/0·75// γ 1·77/0·82/2·06
Ni	up to 40	^{64}Ni	0·03	^{65}Ni	2·59 h	β^- 2·09//γ 1·49/1·12
Cu	0·1	^{63}Cu	2·97	^{64}Cu	12·9 h	E.C./β^+/β^-//γ 1·34
Mo	seldom 2	^{98}Mo	0·03	^{99}Mo	68 h	β^- 1·23/0·45/0·2// γ 0·74/0·18/0·14/0·78/0·36
Cr	up to 20	^{50}Cr	0·73	^{51}Cr	27 d	E.C.//γ 0·32
Fe	chief const.	^{58}Fe	0·0026	^{59}Fe	45 d	β^- 0·26/0·46//γ 1·28/1·1
Ta	1·2	^{181}Ta	21	^{182}Ta	118 d	β^- 0·53/1·1//γ 0·05/1·2
Co	up to 45	^{59}Co	34	^{60}Co	5·2 y	β^- 0·309/1·48//γ 1·17/1·33

It is, however, possible to correct for these interferences by analysis of the composite decay curve.

After irradiation runs of approximately 10 min, integral γ-counting was started after 4 hr, so that short living species such as ^{52}V, ^{66}Cu, ^{51}Ti, ^{94m}Nb, ^{60m}Co, ^{101m}Mo have completely decayed.

The other radioactive species which can be expected in high-alloy steels have half-lives considerably larger than ^{56}Mn so that an analysis of the decay curve causes no serious problem. Exception should, however, be made for ^{65}Ni, with a half-life practically identical with that of ^{56}Mn. The excitation cross-section of ^{64}Ni is, however, quite small (0·03 barn) and in 56% of the disintegration mode no γ-rays are emitted. Experimental results showed that a Ni:Mn ratio of 10 will cause an interference of only 0·1%.

Interfering activities due to the steel constituents can, however, be completely avoided by making use of a pulse-height discriminator set to count only γ-rays with an energy higher than 1·5 MeV. This technique allows a specific counting of ^{56}Mn, as it is the only γ-emitter present in high-alloy steels having an energy higher than this pre-set level. This counting technique makes analysis of the decay curve unnecessary, and thus avoids concomitant errors.

Interference due to (n,p) and (n,α) reactions

Interference from the $^{56}Fe(n,p)^{56}Mn$ reaction, because of the fast neutron flux in the reactor core, can cause an appreciable error, since iron is the main constituent. Although the cross-section of this reaction was determined by Mellish *et al.*,[8] who

reported a value of 0·44 millibarn, it seemed advisible to determine experimentally the reaction yield as a function of the cadmium ratio, the fast flux distribution in the BR-1 reactor not being known with sufficient accuracy. The cadmium ratio can be regarded as a measure of the fast to thermal flux ratio. Cadmium has a cut-off value for neutrons with energy lower than approximately 0·4 eV.

Samples of pure Fe_2O_3 (Johnson Matthey) were irradiated in the reactor core (positions 1 and 2) and in the reflector (positions 3 and 4). The activities due to ^{56}Mn and ^{59}Fe were computed by analysis of the decay curve using a well-type scintillation counter. The cadmium ratios were determined with gold foils (200 mg/cm²) wrapped in cadmium foil (thickness 0·75 mm).

The results expressed as the ^{56}Mn:^{59}Fe count rate ratio at a time t_0 (end of irradiation) as a function of the Cd ratio are represented in Fig. 2.

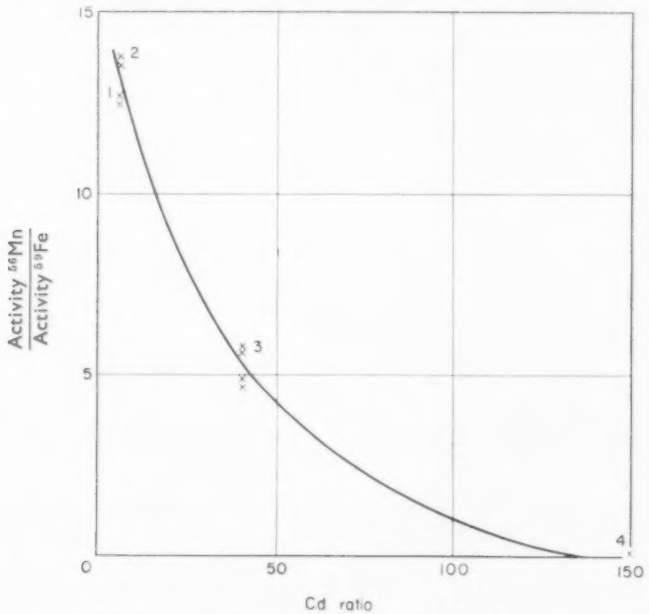

FIG. 2.—$^{56}Fe(n,p)^{56}Mn$ reaction as a function of cadmium ratio.
1, 2—Reactor core
3, 4—Reflector.

Numerical values of thermal and fast neutron fluxes available at the different sites, and measured specific activities of the manganese, are summarised in Table II. The values given are integral counting rates extrapolated at a time t_0 for an irradiation of 1 hr.

Interference from the $^{59}Co(n,\alpha)^{56}Mn$ reaction is also possible when irradiating in the reactor core, as cobalt can occur in large concentrations in high-alloy steels, although the cross-section according to Samsahl *et al.*[9] for the n,α reaction is only 0·14 millibarn.

To determine the extent of this interference, the same technique was used as described for iron, using Co_3O_4 (Johnson Matthey) as target material. After the decay of ^{60m}Co, the activity of the Co samples was followed during several hours but no activity due to ^{56}Mn could be found.

TABLE II

Site	F in n/cm²/sec	Cd ratio	counts ^{56}Mn/min/mg Fe	counts ^{59}Fe/min/mg Fe	$\frac{\text{counts } ^{56}\text{Mn}}{\text{counts } ^{59}\text{Fe}}$
1	$1{\cdot}4\ 10^{12}$	5·3	199	16	12·5
1	$1{\cdot}4\ 10^{12}$	5·3	266	20·8	12·7
2	$8{\cdot}10^{11}$	5·6	148·5	11	13·5
2	$8{\cdot}10^{11}$	5·6	221	16·1	13·7
3	$2{\cdot}10^{11}$	40	14	3·28	4·3
3	$2{\cdot}10^{11}$	40	12·6	3·04	4·1
3	$2{\cdot}10^{11}$	40	25·2	4·46	5·6
3	$2{\cdot}10^{11}$	40	16·3	2·94	5·5
4	$2{\cdot}10^{9}$	150	0	0·028	0

INTERNAL STANDARD ANALYSIS

Leliaert *et al.*[1–3] have already shown that the use of an internal standard allows a correction to be made for self-shielding effects and neutron-flux irregularities. As the neutron-flux gradient in the neighbourhood of site 4 is quite high, it seemed advisible to use this internal standard procedure. Manganese was therefore added to one of the two irradiated samples. The manganese content is given by

$$\% \text{ Mn} = \frac{A_{t_0}(\text{Mn}) \times 100}{a \times S_{t_0}(\text{Mn})} \tag{1}$$

where

$$S_{t_0} = \frac{1}{c}\left[A_{t_0}'(\text{Mn}) \,.\, \alpha - \frac{b}{a} A_{t_0}(\text{Mn})\right], \tag{2}$$

α being given by

$$\alpha = \frac{b}{a}\frac{A_t}{A_t'} \tag{3}$$

where

a and b = weight of samples 1 and 2,
c = weight of manganese added to sample 2,
$A_{t_0}(\text{Mn})$ and $A_{t_0}'(\text{Mn})$ = net manganese activity of samples 1 and 2 respectively at time t_0 (end of irradiation),
A_t and A_t' = rest activity of samples 1 and 2 respectively at a time t after complete decay of the manganese activity.

EXPERIMENTAL

Procedure by integral counting

Two steel samples of approx. 300 mg are accurately weighed. With one of the samples a known amount of approx. 5 mg of manganese (as $MnAc_2{\cdot}4H_2O$) is homogeneously mixed. The samples are pressed in pellets of 5·5 mm diameter and a thickness of approx. 3 mm.

The samples are irradiated in the reflector of BR-1, site 4, during a 10-min period. Integral counting, using a well-type NaI(Tl) crystal is started 4 hr after the end of the irradiation. Counting time is 1 min with 30 min intervals. About 24 hr after the end of the irradiation the manganese activity can be considered as negligible, allowing the computation of the correction factor α from the activity of the long living species.

Two typical decay curves (235/I 18–8 and 155) are given in Fig. 3, from which it appears that the analysed half-life of ^{56}Mn is in good agreement with the expected value of 2·58 hr.

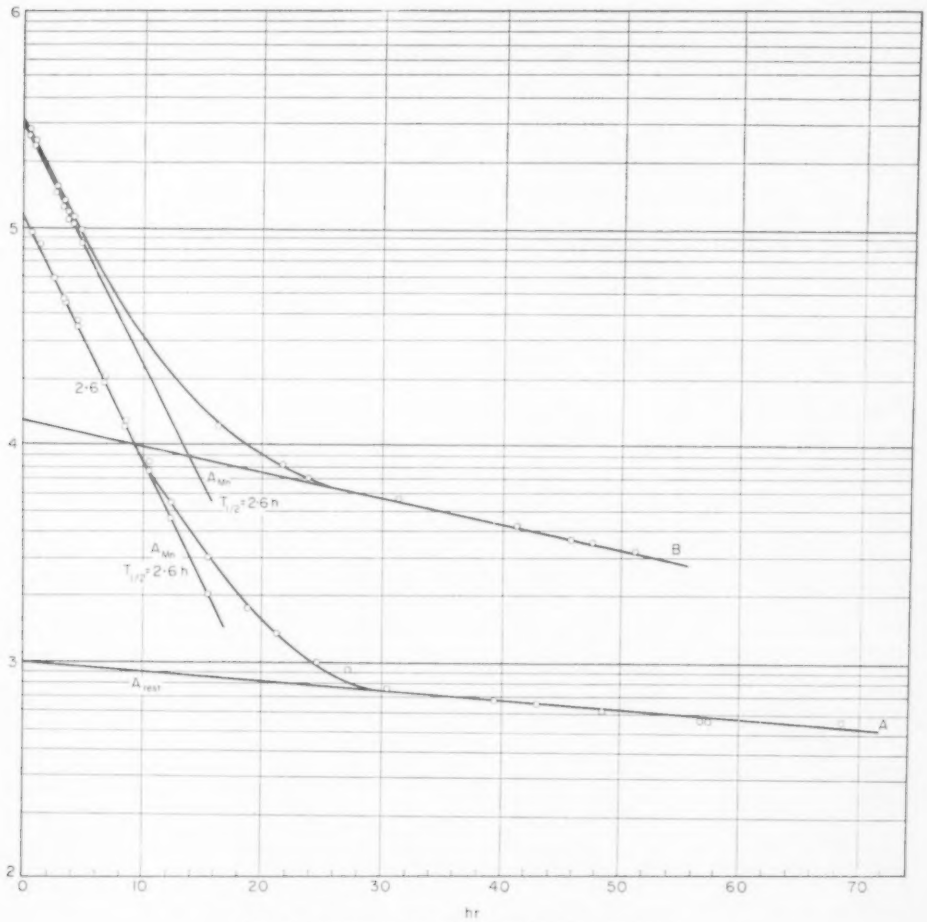

FIG. 3.—Decay curves of steel 235/I and steel 155.
A—231/I, 18/8′
B—155.

Analyses of a number of British Chemical Standard and National Bureau of Standard Steels are summarised in Table III.

From Table III it appears that the results obtained by activation analysis are in excellent agreement with those obtained by careful chemical analysis, giving approximately the same standard error.

Procedure by pulse height discrimination

Steel samples prepared as described above were measured with a well-type NaI(Tl) crystal coupled to a pulse height discriminator and counter. The pulse height discriminator was set to measure only gamma's with energy higher than 1·5 MeV. In this condition ^{56}Mn is measured specifically in the

TABLE III.—ACTIVATION ANALYSIS OF Mn

Sample	% Mn given	% Mn found
BCS 235/1	0·60 ± 0·017	0·608 ± 0·03 (18)‡
NBS 155	1·25 ± 0·015*	1·235 ± 0·027 (16)
	1·24 ± 0·01†	
NBS 101d	0·739 ± 0·004	0·795 ± 0·008 (12)
		0·748 ± 0·014 (9)

* Bismuthate method.
† Persulphate method.
‡ Number of analyses between brackets.
BCS 235/1: 18·3% Cr; 8·21% Ni; 0·36% Ti; 0·6% Si.
NBS 155: 0·485% Cr; 0·517% W; 0·1% Ni.
NBS 101d: 18·68% Cr; 9·05% Ni.

presence of the other activated steel constituents, as appears from the decay curves obtained from different standard steels (see Fig. 4).

About 24 hr or more after the end of the irradiation, the correction factor α is computed from the integral count-rate of the long lived species.

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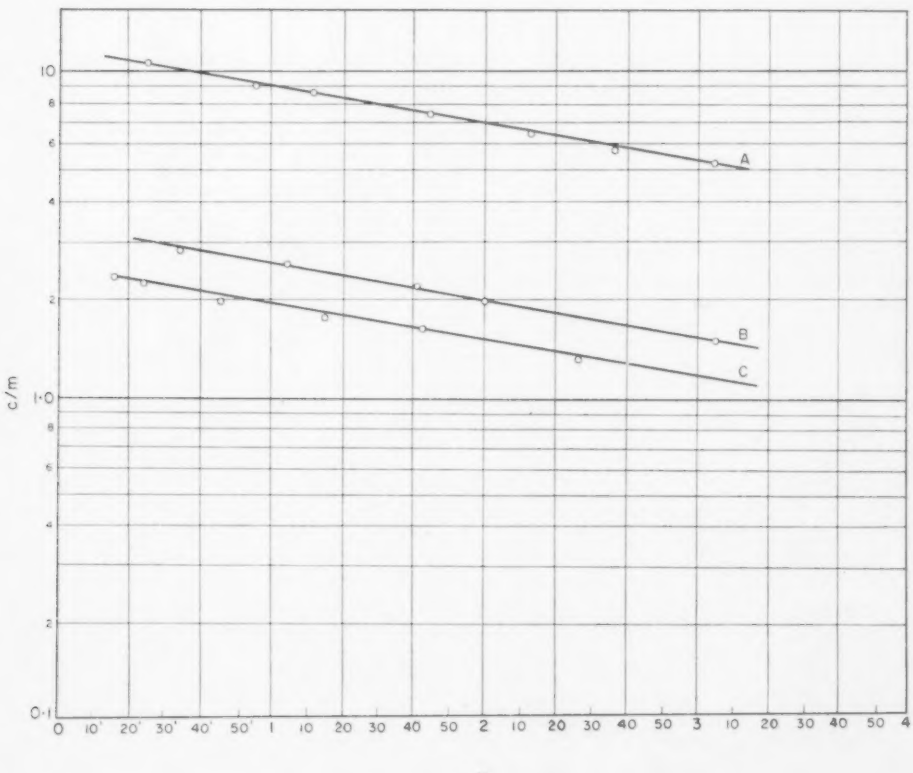

FIG. 4.—Decay curves of ^{56}Mn.
A—PMA 266: $T_{1/2}$ = 2 hr 32 min.
B—NBS 155: $T_{1/2}$ = 2 hr 32 min.
C—NBS 101d: $T_{1/2}$ = 2 hr 37 min.

The results of a series analyses of NBS steel 101d (Mn 0·739%; Cu 0·184%; Ni 9·05%; Cr 18·68%; V 0·049%; Mo 0·11%; Co 0·058%) are represented in Table IV.

TABLE IV. ACTIVATION ANALYSIS OF NBS STEEL 101d

Sample weight, *mg*			α	% Mn
a	b	c		
319·36	312·39	5·232	1·071	0·762
320·25			1·486	0·760
282·10			0·928	0·742
305·83			1·193	0·751
319·36	342·81	5·359	1·091	0·777
320·25			1·512	0·775
282·10			0·944	0·757
305·83			1·214	0·766
319·36	317·86	4·877	1·032	0·747
320·25			1·432	0·745
282·10			0·894	0·727
305·83			1·149	0·736
319·36	268·29	5·115	0·618	0·733
320·25			0·857	0·731
282·10			0·535	0·713
305·83			0·688	0·722
			Average:	0·747 ± 0·021
			Stand. dev.:	2·8%

Although all samples were irradiated simultaneously in the Lucite container illustrated in Fig. 5, it appears that a considerable variation in the correction factor occurs, since it varies from 0·5 to 1·5.

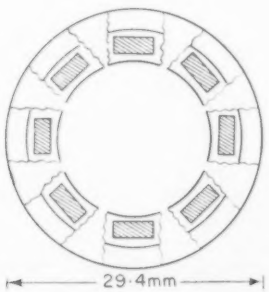

FIG. 5.—Diagram of the Lucite container.

Results of the analyses of other steel standards are represented in Table V, giving evidence that the method is applicable to widely varying steel samples.

The results of Table V appear to have the same accuracy and precision as those obtained by integral counting. In fact, for small manganese contents the standard errors are not larger than those computed from the certificates.

TABLE V. ACTIVATION ANALYSIS OF Mn IN HIGH-ALLOY STEELS

Sample	% Mn given	% Mn found
BCS steel 266 *PMA* Co: 23·4% Ni: 13·3% Al: 7·95% Cu: 3·3% Ti: 0·1% Fe: 49·7%	0·27 ± 0·012*	0·276 ± 0·005 (9)†
BCS steel 233 *PMA* Co: 23·7% Ni: 11·2% Al: 6·98% Cu: 5·09% Fe: 51·15%	0·235 ± 0·005	0·245 ± 0·017 (12)
NBS 155 Cr: 0·485% W: 0·517% Ni: 0·1%	1·25 ± 0·015 1·24 ± 0·01	1·24 ± 0·050 (20)
NBS 101*d* Cr: 18·68% Ni: 9·05%	0·739 ± 0·004	0·746 ± 0·021 (16)
BCS cast iron 149 S: 0·011% P: 0·010%	0·023 ± 0·0018	0·025 ± 0·001 (28)

* Standard deviation from certificates.
† Number of analyses in brackets.

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Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Mangan in Gusseisen und Stählen herangezogen. Selbstabschirmung sowie irregulärer Fluss der Neutronen wurden durch Verwendung eines internen Standards als Fehlerquellen ausgeschaltet. Zwei Methoden, integrale Zählung und Messung der Impulsstärke wurden angewandt. Resultate an Proben mit weit wechselnden Mangangehalten, zeigten vorzügliche Übereinstimmung mit denen nach klassischen, chemischen Methoden erhaltenen.

Résumé—Les auteurs ont mis au point une méthode d'analyse par activation pour le dosage du manganèse dans la fonte et dans les aciers spéciaux. Les erreurs d'auto-protection et les irrégularités du flux de neutrons sont évitées par l'utilisation d'un étalon interne. Deux procédés sont utilisés: comptage intégral et mesure de la hauteur des impulsions. La méthode a été essayée sur des échantillons étalons. Les résultats obtenus sur des échantillons avec une composition très différente sont en très bon accord avec ceux obtenus par l'analyse chimique classique.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH NITROSO R-SALT

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Summary—A procedure is outlined for the spectrophotometric determination in the visible light region of palladium^{II} with nitroso R-salt. The absorbance of the red organo-palladium complex is measured at 510 mμ; the optimum pH range is 2 to 2·6. The colour reaction is instantaneous, and the complex formed is stable for several days and obeys Beer's law. The tolerance to a number of ions has been established, and palladium can be determined, even in the presence of gold, with good precision and accuracy.

INTRODUCTION

AMONG the various procedures for the spectrophotometric determination of palladium, the method proposed by Cheng[1] using 2-nitroso-1-naphthol seems to be a relatively simple one. This method, however, requires the extraction of the palladium complex into toluene. It seemed to the authors that in order to avoid the extraction step a sulphonic derivative of a similar compound could be used for such a procedure. It is the purpose of this paper to present such a method, using nitroso R-salt (sodium 1-nitroso-2-naphthol-3,6-disulphonate).

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman spectrophotometer model DU, using matched 1·00-cm Corex cells.

All pH measurements were made with a Photovolt glass electrode pH meter model 100.

Reagents

Nitroso R-salt, 0·02M aqueous solution: Prepared from B.D.H. material. The solution is stable for several months.

Palladium solution: Dry purified palladium^{II} chloride (Fisher) was dissolved in 0·25*M* hydrochloric acid to give a 0·01*M* solution of palladium. The standardisation was made gravimetrically by precipitating with β-furfuraldoxime.[2] Four analyses were in good agreement and gave an average of 1060 ppm of palladium. The solution was then diluted with distilled water to 0·0002*M* or 21·34 ppm of palladium.

Reagent grade salts were used to prepare solutions of the various other ions.

Absorption spectra

The addition of 1 drop of the reagent solution to 1 drop of palladium solution causes a red colour to be formed at once. In Fig. 1 the absorption spectra of the red coloured complex and of the reagent itself are shown. The maximum absorbance of the complex is at 430 mμ and there is a plateau at 500–510 mμ. Since the reagent itself has a significant absorbance at 430 mμ we preferred to make our measurements at 510 mμ where the absorbance of the reagent is negligible and a water blank is satisfactory.

Effect of pH

The best results were obtained when acetic acid was present at 0·2*M* concentration and the pH was about 2·6 (Fig. 2, curve I). A calibration curve of smaller slope was obtained in the presence of hydrochloric acid at 0·01*M* concentration and the pH was about 2 (Fig. 2, curve II). In cases where

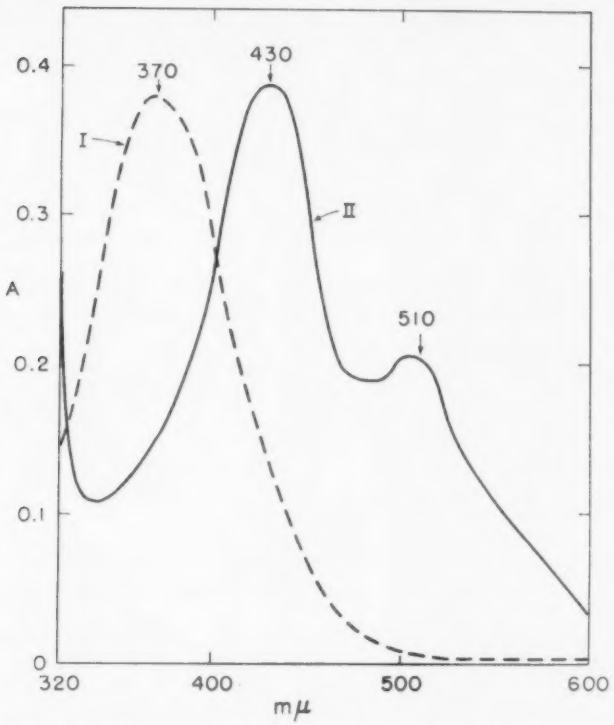

FIG. 1.—Curve I: Spectrum of a solution of nitroso R-salt at a concentration of 6×10^{-4} *M* in water. Length of path, 0·1 cm.
Curve II: Spectrum of a solution of 1·0 ml of 0·0002*M* $PdCl_2$ + 2·0 ml of 0·0002*M* nitroso R-salt + 1·0 ml of 0·1*M* HCl + 6·0 ml of water. Length of path, 1·0 cm.

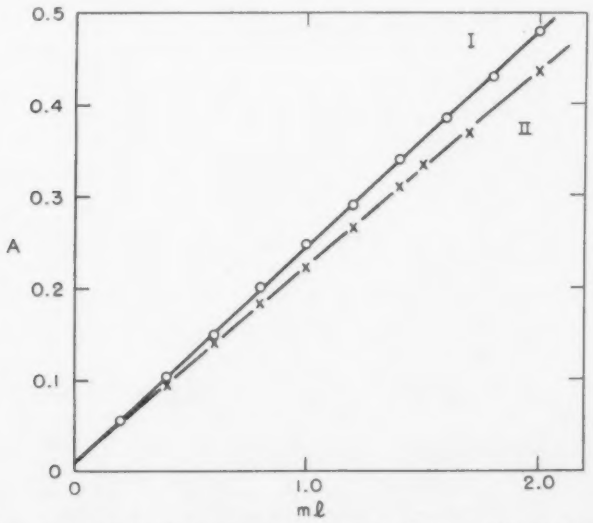

FIG. 2.—Curve I: Calibration curve; absorbances of solutions with 1 ml of 0·002*M* nitroso R-salt + 2 ml of 2*M* CH_3COOH + X ml of 0·0002*M* $PdCl_2$ + (7-X) ml of water.
Curve II: Calibration curve; absorbances of solutions with 1 ml of 0·002*M* nitroso R-salt + 1 ml of 0·1*M* HCl + X ml of 0·0002*M* $PdCl_2$ + (8-X) ml of water.

acetic acid might form complexes with other ions present it would be preferable to use hydrochloric acid.

Concentration of reagent

It is desirable to use an excess of the reagent, since the absorbance of the solution is increased somewhat by increasing the concentration of the reagent. For a sample solution of total volume 10·0 ml, we used 1·0 ml of 0·002*M* nitroso R-salt solution, and the amounts of palladium varied between 0·2 ml and 2·0 ml of 0·0002*M* solution.

Beer's law

In Fig. 2 are represented two calibration curves. In curve I the pH is adjusted by using 2·0 ml of 1*M* acetic acid in a sample of total volume 10·0 ml. The molar absorptivity is $\alpha = 1{\cdot}2 \times 10^4$.

In curve II the pH is adjusted by using 1·0 ml of 0·1*M* hydrochloric acid in a sample of total volume 10·0 ml. The molar absorptivity in this case is $\alpha = 1{\cdot}1 \times 10^4$.

Beer's law is obeyed over the concentration range tested, *viz.*, up to 4·27 ppm of palladium, the most sensitive range being 1·28 ppm to 4·27 ppm, which gives absorbances of 0·141 to 0·450.

Stability

The colour is formed immediately and is constant when measured 15 min after preparation or at any time afterwards within 24 hr.

Tolerance to diverse ions

The interferences of platinum, rhodium, osmium and gold were checked. Solutions which contained 2·13 ppm of palladium and 20 to 40 times as much of the above mentioned elements did not show any significant interference. However, the absorbance of the solutions containing $HAuCl_4$ changed slowly with time. Therefore, the absorbances had to be measured within 1 hr after preparing the solutions. The best results were obtained when a blank solution, containing the same materials except for palladium, was prepared simultaneously. By doing so the differential absorbance was constant over a period of almost 2 hr. When other elements were present the absorbance could be measured even after 1 day.

DISCUSSION

The use of nitroso R-salt for the determination of small amounts of palladium has several advantages. The complex formed is soluble in water, and no extraction is required; the colour reaction is rapid and is stable; the stock solution is stable over a long period of time; the pH for maximum absorbance is easily controlled. It allows a high tolerance for several ions, and this is most important in the presence of gold, which, when using other methods, has to be removed before the determination of palladium. It is a rapid, sensitive, and precise method. Since the colour of the complex is red, the method can probably be easily adapted for colorimetric determinuoiɹɐ.

Zusammenfassung—Eine Methode zur spectrophotometrischen Bestimmung von Palladium(II) mit Nitroso-R-Salz im sichtbaren Bereich wird mitgeteilt. Die Absorption des roten Palladiumkomplexes wird bei 510 mμ gemessen. Der optimale pH-Bereich ist 2-2·6. Die Reaktion verläuft momentan, die Farbe ist über Tage hinaus beständig und Beer's Gesetz ist erfüllt. Der Einfluss einiger Ionen wurde studiert. Palladium kann selbst in der Gegenwart von Gold genau bestimmt werden.

Résumé—Les auteurs donnent un aperçu d'un procédé de dosage spectrophotométrique dans le visible du palladium II par le sel nitroso-R. L'absorption du complexe organique rouge du palladium est mesurée à 510 mμ; le domaine de pH le meilleur est 2-2,6. La réaction colorée est instantée, le complexe formé est stable pendant plusieurs jours et obéit à la loi de Beer. La tolérance pour un certain nombre d'ions a été établie, le palladium peut être dosé avec une bonne précision, même en présence d'or.

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NEW METHODS OF INORGANIC ULTRAMICROANALYSIS UNDER THE MICROSCOPE

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Summary—The results of investigations carried out by the authors in the field of ultramicroanalysis on the stage of a microscope are presented. The peculiarities of ultramicromethods are considered in detail, and the new techniques of experimentation in qualitative and quantitative ultramicroanalysis are described: electrolysis with platinum and mercury electrodes, potentiometric and amperometric titration, and separation of metals by means of ion-exchange resins. The results of the determination of a number of elements by various ultramicroanalytical methods are given.

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ULTRAMICROCHEMICAL analysis is a comparatively new development in analytical chemistry which enables the problem of investigating very small amounts of substance to be solved.

There are now two trends in ultramicroanalysis, depending on the quantities of substance investigated, which determine the manipulative technique. On the one hand, simple mechanical devices are used when manipulating with volumes of $n \times 10^{-3}$ ml, and the majority of chemical procedures are observed with the unaided eye or with the aid of a magnifying glass; on the other hand, with volumes less than 10^{-3} ml, all the main chemical procedures are carried out on the stage of a microscope with the use of micromanipulators. The practical techniques of experimentation for the first trend have been developed by P. Kirk's (U.S.A.), and I. Korenman's (U.S.S.R.) schools.

The most general apparatus for chemical experimentation on the stage of a microscope with the use of micromanipulators, and the technique of working, became known due to the work carried out by A. A. Benedetti-Pichler and his co-workers (U.S.A.). Later this trend has been fruitfully developed by C. L. Wilson's (Gt. Britain) school.

The aim of our investigations was the further development of the technique and methods of experimentation for this trend, to make possible the use on this scale of the most widely used methods of analysis. We considered it expedient to choose this particular trend for systematic study from the point of view of utilising more completely the possibilities of the ultramicromethod for the investigation of small samples.

PECULIARITIES OF THE ULTRAMICROMETHOD OF CHEMICAL ANALYSIS

Chemical determinations with small amounts of material can be carried out by ultramicroanalysis, while maintaining the usual concentrations of the reacting substances, by decreasing the volume of the solution correspondingly. This results in the increase (in comparison with the macro method) of the relative surface of the

solution and the vessel, *i.e.* in the increase of surface per unit volume, owing to the fact that surface decreases to a lesser degree than volume. This is shown in Table I.

Because of the relatively greater area of contact with the walls of the vessel, dissolved substances are adsorbed by these, and attack the walls to a greater extent than in the macro method.

TABLE I.—RATIO OF RELATIVE SURFACES

Method	Diameter of the vessel, *cm*	Height of the vessel, *cm*	Surface of the vessel, cm^2	Volume of the solution, cm^3	Relative surface, S	$\frac{S_u}{S_m}$
Macro method	4·0	4·0	62·5	50·0	1·25	>20
Ultramicro method	0·2	0·2	0·16	0·006	26·6	

When working on the ultramicro scale, the free surface of liquid is also relatively larger, because of the curvature of the meniscus in capillaries.[1] So the speed of evaporation of solutions, which is directly proportional to the free surface of liquid, reaches a considerable value. Obviously, liquids moistening a capillary have a considerably lower vapour pressure in it than in wide vessels, because of the larger curvature of the concave surface. Nevertheless, the evaporation goes on much faster, since the relative increase of the free surface is considerably larger than the decrease of vapour pressure. For example, the free surface of liquid in a capillary of 0·6 mm diameter is not equal to 0·3 mm^2, as is the flat surface, but is about 0·6 mm^2, whereas the vapour pressure above the meniscus of the corresponding curvature decreases only by 5%. In addition, the solution in a capillary is in considerably better condition from the point of view of heat transfer. In order to diminish the speed of evaporation of liquids from capillaries, a method of working in a humid atmosphere is used; in this case the speed of evaporation from comparable volumes decreases by 10–15 times.

Aqueous solutions of salts, having lower vapour pressure than water, evaporate, other things being equal, more slowly than water, but not to such a degree that the necessity of working in a humid atmosphere is eliminated. When working in a humid atmosphere, the volume of saturated salt solutions increases because of the equalisation of vapour pressure in the system, Vapour above pure water (humid atmosphere)—Vapour above a saturated solution in a capillary. The hygroscopicity of the dissolved compound is also of importance. For example, comparable volumes of a saturated calcium chloride solution in a humid atmosphere increase about 30 times faster than in a normal atmosphere. Therefore it is not advisable to work with saturated solutions of salts and concentrated acids in a humid atmosphere.

The relative increase of the surface of a liquid in comparison with its volume results in an increase of adsorption of substances from solutions and of the speed of evaporation as well as in an increase of surface tension, which reaches considerable values when working in capillaries. This must be taken into consideration first of all when the experimental technique for an ultramicromethod is being developed. On the one hand, the situation is more complicated because of the necessity of overcoming the surface tension when the liquid is transferred from one capillary to another. On the other hand, this eliminates losses of the solution through spilling, and permits the exact measurement of solutions, because of the stable (within the limits of the speed of evaporation) position of the meniscus.

Solutions of salts, as is known, have a greater surface tension than water; the tension increases almost in proportion to the number of equivalents of the dissolved salt. The creeping of salts (for example, ammonium chloride), which is a serious hindrance when working in capillaries, can be explained by the increase of surface tension.

To eliminate, to a considerable degree, a number of the effects connected with the large surface of contact of the solution with the walls of the vessel, and with the use of capillaries, we suggest coating the walls of a micro vessel by a layer of an organosilicon compound.[2]

The glass surface coated with a methylchlorosilane film is not moistened by water solutions; this makes possible manipulation with them without washing the vessel. When working with such vessels the titration error connected with the speed of the solution flowing out of a horizontal burette is reduced to zero.

The hydrophobic surface is poorly moistened by water solutions because of the decrease of surface tension on the border between this surface and the solution. This is why such phenomena as the creeping of salts to the outside walls of capillary vessels, and of calomel micro electrodes, can be eliminated by making them hydrophobic (Fig. 1*a*).

The free surface of liquid in capillary vessels treated with the solution of an organosilicon compound decreases considerably owing to the flattening of the meniscus (Fig. 1*b*). Because of this, the speed of evaporation from such vessels decreases considerably (approximately by 25%). In addition, the measurement of volumes in burettes and vessels using the flat meniscus is more simple and accurate.

Owing to the greater value of the $\frac{S}{V}$ ratio in the ultramicro method, special attention must be paid to the possibility of losing the substance by adsorption, even from solutions of usual concentration. Investigations carried out with radioactive isotopes showed that losses of substance by adsorption are considerably less when working in vessels with hydrophobic walls.

Special consideration must be given to the problem of observation of the colour of solutions in coloriscopic capillaries.[1] A mean sensitivity for a number of colour reactions is 10^{-8} g in 1 ml. In ultramicro methods (with volumes of 10^{-3}–10^{-4} ml) the sensitivity may be as high as 10^{-12} g.

Assuming that the Bourguer-Lambert-Beer law, $E = kcl$, is valid for immeasurably small concentrations of substance, a minimum concentration for a certain reaction should be quoted only in a layer of a given thickness. Only in this sense has the notion of "minimum concentration" a precise meaning.

For a given coloured substance (K = const.) the product $cl = E$ is constant. It follows that the minimum concentration value is determined by the nature of the coloured substance and the chosen length of the light path; it does not depend on other values, in particular, on the cross-section of the layer of liquid.

The sensitivity of a reaction, in addition to the minimum concentration, is determined also by the identified minimum

$$m = c_{min} \cdot v = c_{min} \cdot \underset{chosen}{l} \cdot s \quad ,$$

that is, the identified minimum is proportional to the cross-section of the layer of liquid.

The thickness of the layer of a coloured solution in coloriscopic capillaries is comparable with that in the macro method, whereas the cross-section is considerably less. This makes it possible essentially to decrease the identified minimum. The cross-section of the layer of liquid in the ultramicromethod is usually 10^{-4} times that in the macro method. Hence, the detected minima of elements determined are in the same ratio.

The limiting concentration per unit length, which does not depend on the cross-section of the column of liquid, when the layer thicknesses are comparable, is the same for the macro and ultramicro method.

It has been confirmed by our experimental results that the identified minimum depends on the cross-section of the layer of a coloured solution. Thus, in the macro method when the cross-section of the solution layer is 1 cm^2, the identified minimum for iron is 10^{-5} g, whereas in the ultramicro method it is 10^{-9} g.

QUALITATIVE AND QUANTITATIVE ULTRAMICROANALYSIS

According to the literature, there are now a number of methods and suitable apparatus for qualitative and quantitative analysis on the stage of a microscope.

No attention, however, has been paid to chromatographic separation in small volumes, to electrochemical methods of separation and determination, or to the physicochemical determination of the end-point in titration. This limits the possibilities for investigation by an ultramicrochemist of small amounts of substance.

The following is the description of some new apparatus and methods for analysis on an ultramicro scale.

Chromatographic separation in small volumes

Chromatographic separation used as an ultramicro method has a great advantage over other methods of separation, because the separated elements can be often obtained in a very pure state without introducing into the solution a reagent which is difficult to remove. As well, the process of separation on the ultramicro scale takes considerably less time because of working with small volumes of solutions and the use of small amounts of sorbent (0·05–0·1 g).

The ultramicro technique of chromatographic experimentation has no difference in principle from the usual one. But the work with small volumes inevitably affects the apparatus and the methods of manipulation.

We propose the use for this purpose of a column which consists of a thin-walled capillary of 2 to 2·5 mm diameter and 3 to 4 cm long with a drawn out end and a porous glass partition. The solution is forced out of the column by the pressure created by a levelling bulb. The eluates are collected in microvessels of 1·5 to 2·0 mm diameter. The vessels are placed in a circle on a rotating cylindrical stand-holder. Solutions are introduced into the column by a micropipette (Fig. 2).

Iron and nickel, chromium and vanadium were separated by this method in volumes of $1{\cdot}2 \times 10^{-3}$ ml in quantities of $0{\cdot}5 \times 10^{-6}$ to 1×10^{-6} g.

Electrochemical separation and identification of elements

Electrochemical analysis under the microscope can be carried out by means of the special apparatus constructed by the authors.[3]

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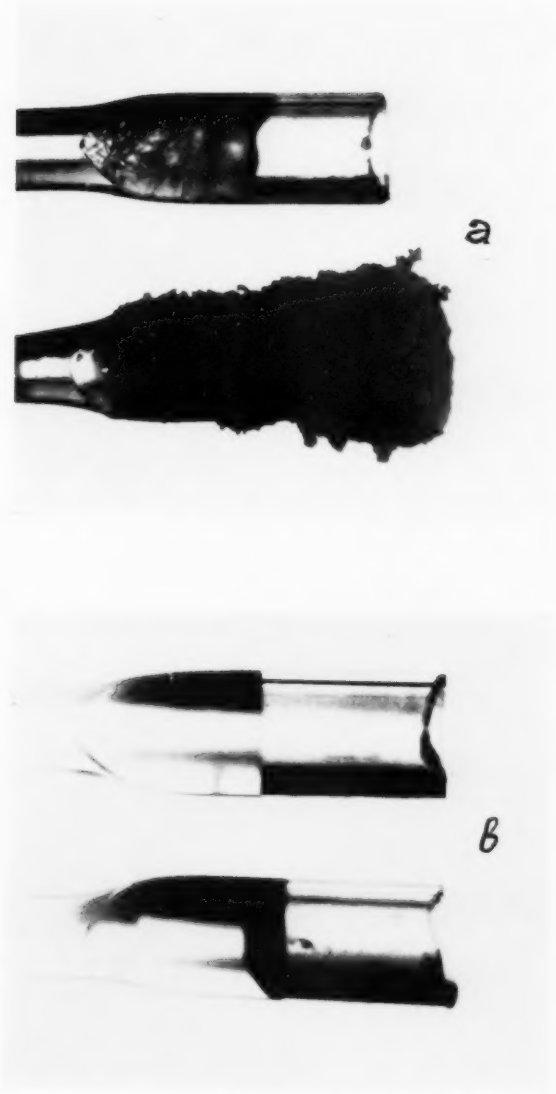

FIG. 1.—Effect of hydrophobisation of the walls of micro vessels.

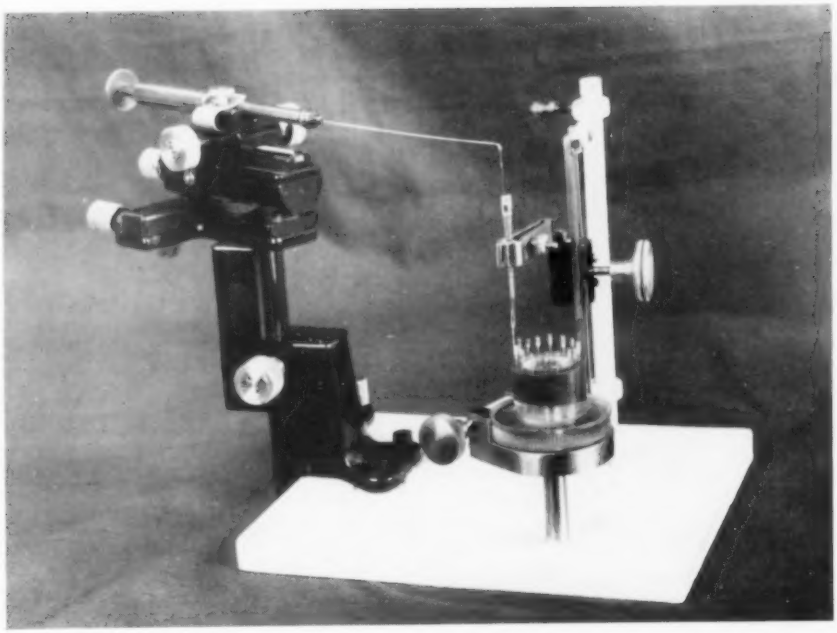

FIG. 2.—Chromatographic column (1/3–1/4 natural size).

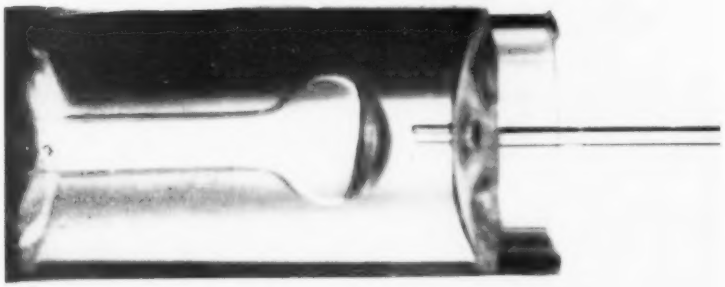

FIG. 7.—Microcell with a glass electrode.

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For obtaining a certain current density (0·1–0·01 A/cm²) it is necessary to have a current strength of 10^{-4} to 10^{-5} A, because of the small surface of the electrodes used in the ultramicro method. The apparatus is different from that for macro electrolysis (a micro cell is used).

The cells used for electrolysis with platinum electrodes were of two types:

(a) The electrolyte is placed on a platform in a thick-walled capillary in the form of a condenser rod which has a platinum wire about 0·2 mm in diameter welded into its channel; the end of the wire which is in the platform plane serves as the anode.

The cathode consists of a platinum wire welded to a flexible wire which passes through the capillary and the ebonite holder. There is a terminal at the end of the flexible wire to connect to the source of current (Fig. 3*a*).

(*b*) The electrolyte is placed in a microvessel into which the platinum electrodes are inserted. The electrodes consist of isolated platinum wires 0·1–0·2 mm in diameter welded into a capillary. The electric current is fed through thin flexible wires one end of which each of these being welded to the platinum wire and the other to the terminals of the ebonite holder (Fig. 3*b*).

Using the apparatus described, it is possible to isolate and identify 10^{-6}–10^{-8} g of a metal in a volume of 10^{-3}–10^{-4} ml, the electrode surface being equal to about 10^{-4} cm².

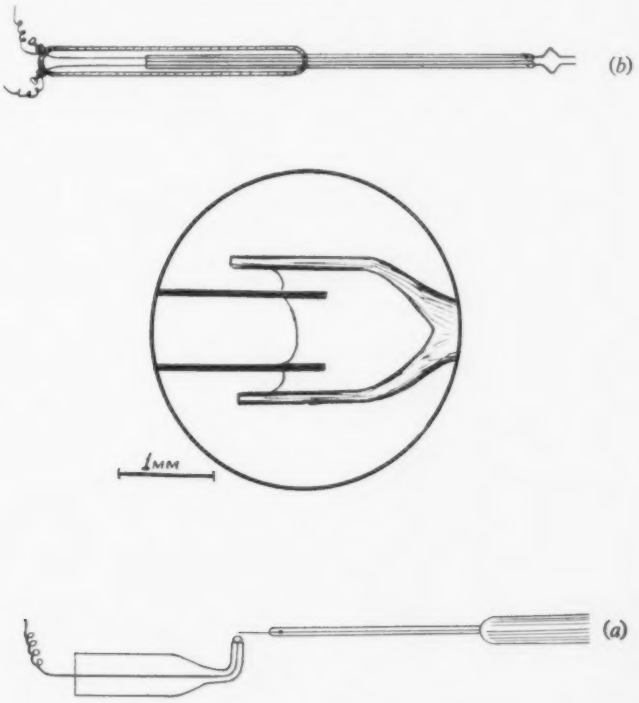

FIG. 3.—Electrolytic micro cells with platinum electrodes.

Electrolysis on a mercury cathode is carried out in a capillary with both ends open because of the intense gas-generation during the electrolysis, because of which the solution is ejected from an ordinary vessel.

The mercury cathode is made by electrodepositing mercury on a platinum fork which serves as cathode in the electrolysis (Fig. 4).

After deposition of the metal on the mercury cathode, the mercury may be removed by connecting the cathode in the circuit to a micro heater. Mercury having been removed, the metal remaining on the fork is dissolved by immersing in a suitable solvent in a micro cone, and it is then identified in the solution by a sensitive reaction.

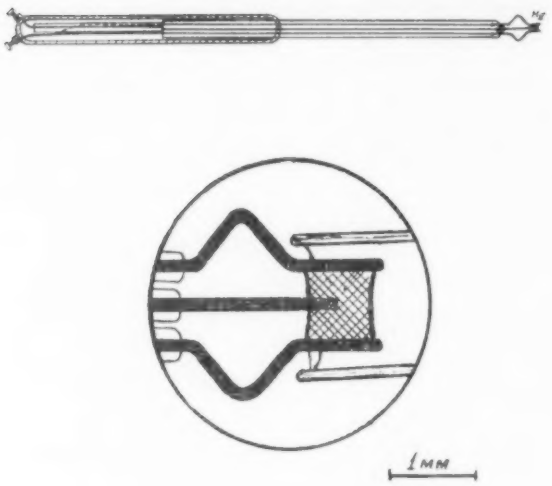

FIG. 4.—Mercury micro cathode.

It is possible to deposit 10^{-6}–10^{-7} g of a metal on a mercury cathode of 2×10^{-3} cm² surface from a volume of solution of about 10^{-3} ml, in 15–20 min.

Some of the results of the qualitative identification of a number of elements obtained during the development of the method are given in Table II.

TABLE II.—QUALITATIVE IDENTIFICATION OF SOME ELEMENTS

Element	Reagent	Limit of identification, *g*	Method of identification
Ag	Potassium chromate	1×10^{-9}	Microcrystalloscopy
Fe	Potassium thiocyanate	2×10^{-9}	Coloration in the coloriscopic cuvette
Cr	Diphenylcarbazide	3×10^{-12}	Coloration in the coloriscopic cuvette
Ni	Dimethylglyoxime	1×10^{-8}	Precipitate
Cu	—	5×10^{-8}	Electrolysis
Pb	—	5×10^{-7}	Electrolysis

Titrimetric ultramicroanalysis

More precise titration and decrease in the drop error is possible in ultramicrotitration by using electrometric methods for the determination of the equivalent point.

But the wide use, for example, of *potentiometric titration* in ultramicro titrimetric analysis is hindered by a number of specific difficulties in connection with the investigation of very small volumes.

We recommend, as a cell for potentiometric titration, a capillary vessel of 1–2 mm diameter with a platinum wire welded into it, and a reference calomel electrode with a capillary end. The burette is also a capillary of about 0·5-mm bore, the end of which is drawn down to 0·02 mm in diameter. Such a burette works as a micropipette, but with the possibility of the exact measurement of solutions. To carry out the measurement a dial micrometer placed between the micrometer screw and the holder,

of which the moving part works as a plunger, is used. In this case, a certain number of scale divisions, recorded by the micrometer scale pointer when the screw is turned, corresponds to a certain volume of solution when the burette is filled or emptied. This volume is easily measured by calibrating the burette.

The mixing of solution during the titration can be suitably performed by a nitrogen current which is fed through a tube with a capillary end directed to the surface of the liquid. The gas current causes turbulent motion of the liquid in the vessel.

To carry out the titration, a vessel with the indicator electrode, and a holder with the necessary vessels, are placed into the moist chamber on the stage of the microscope. The burette, the calomel electrode, and the tube to feed the mixing gas, are clamped in three manipulators placed to the right of the microscope (Fig. 5). Turning the vessel to each of the manipulators in succession, the titrant is

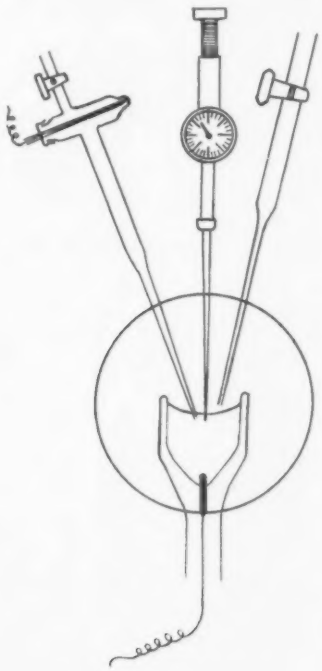

FIG. 5.—Cell for potentiometric ultramicro titration.

added, the solution is mixed, and the potential value is measured. Titrating $0{\cdot}5–1{\cdot}5 \times 10^{-3}$ ml with $0{\cdot}1–0{\cdot}01N$ solutions, $10^{-6}–10^{-7}$ g of an element can be determined with an accuracy of 0·5–3%.[4]

For *amperometric ultramicro titration* on the stage of the microscope, the following apparatus and method are used. The indicator electrode is a vibratory platinum wire, 0·2 mm in diameter and 2–3 mm long. The reference electrode is a saturated calomel electrode with a capillary end.

Titration can be suitably performed in a capillary microvessel, and the titrant can be added by the burette with a dial micrometer screw.

The micro vessel on the holder is placed on the stage of the microscope in a moist chamber with a cross slot in its side wall. Through this slot a vibratory electrode is inserted into the chamber. The electrode is set in the clamp of the manipulator perpendicular to the two other manipulators which are placed, as usual, to the right and the left of the microscope. The burette and the reference electrode, with ends bent to a right angle, are clamped in these manipulators (Fig. 6). As the titrant is added, the galvanometer deflection is recorded, and the corresponding volume of the titrant is measured by the burette scale. From 10^{-7} to 10^{-8} g of an element can be determined amperometrically in $0{\cdot}5–1{\cdot}5 \times 10^{-3}$ ml of $0{\cdot}01–0{\cdot}001N$ solution. The accuracy of the determination is about 1%.[5]

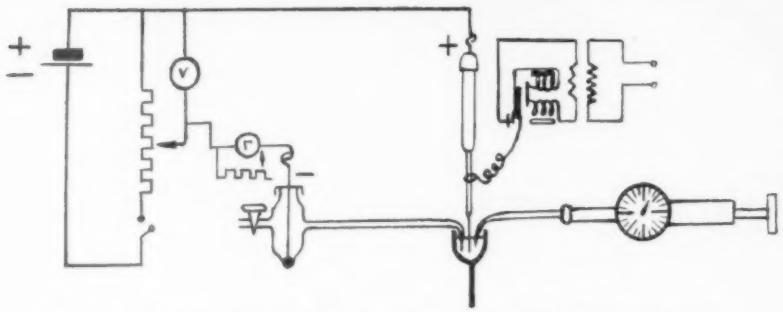

FIG. 6.—General diagram of the apparatus for amperometric ultramicro titration.

A glass electrode with a bulb about 0·3 mm in diameter, made in the microflame of a special glass capillary, is used for *measuring the pH* of solutions in volumes of about 10^{-3} ml. The glass and calomel electrodes are placed in the right and left manipulators, brought into the field of vision of the microscope, and immersed in the solution contained in the section of the capillary on the microscope stage (Fig. 7). Tests of such a micro cell with buffer solutions, in comparison with measurements made using a standard cell, showed a satisfactory reproducibility of pH values within 1–3% of the value measured.

The results of some quantitative determinations carried out by means of the methods developed, are given in Table III.

TABLE III. QUANTITAVE ULTRAMICRO DETERMINATIONS

Element	Taken, *g*	Found, *g*	Error %	Method
Cr	$1{\cdot}73 \times 10^{-7}$	$1{\cdot}733 \times 10^{-7}$	+0·2	Potentiometric titration
Fe	$0{\cdot}56 \times 10^{-6}$	$0{\cdot}57 \times 10^{-6}$	+2·0	
V	$5{\cdot}1 \times 10^{-7}$	$5{\cdot}22 \times 10^{-7}$	+2·3	
Cl	$3{\cdot}3 \times 10^{-7}$	$3{\cdot}27 \times 10^{-7}$	−1·0	
V	$2{\cdot}55 \times 10^{-8}$	$2{\cdot}53 \times 10^{-8}$	−0·8	Amperometric titration
V	$5{\cdot}2 \times 10^{-8}$	$5{\cdot}24 \times 10^{-8}$	+1·0	
Mg	$5{\cdot}5 \times 10^{-9}$	$5{\cdot}8 \times 10^{-9}$	+7·0	Colorimetry
S	$7{\cdot}7 \times 10^{-8}$	$8{\cdot}08 \times 10^{-8}$	+5·0	
K	$3{\cdot}3 \times 10^{-8}$	$3{\cdot}1 \times 10^{-8}$	−6·0	By the volume of the precipitate

In conclusion we should like to add that the techniques of experimentation either known before or described here have been used to investigate various small samples (inclusions and very small parts of meteorites, cell sap of plankton diatoms,[6] various thin coatings, corrosion products *etc.*)

This has shown that the analysis of small amounts of substance can be carried out on the stage of a microscope. The investigation may be as complete as the investigation of large quantities of substance on the macro scale.

In addition, ultramicro methods may be applied to the analysis of any materials for impurities, on condition that a method for removing the main component (or for isolating the admixtures) is found, which will permit concentration of the admixtures in a small volume.

Zusammenfassung—Neue Geräte und Techniken wurden entwickelt um einige Ultramikroanalysen durchzuführen. Es wurde gezeigt, dass die Analysen unter einem Mikroskop durchgeführt werden können. Die Analysen können genau so komplet sein wie solche, die im Makromasstab vollzogen werden.

Résumé—Les auteurs ont mis au point un appareil et des techniques expérimentales pour un certain nombre de méthodes ultramicrochimiques. Ils ont montré que l'analyse de faibles quantités de substance peut être réalisée à l'aide d'un microscope. Cette étude peut être aussi complète que l'étude de quantités importantes de substances à grande échelle.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—III

THE DETERMINATION OF INDICATOR CONSTANTS AND THEIR USE IN THE CALCULATION OF SCREENING CONDITIONS

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Summary—It is shown that the indicator constants of acid-base indicators can be calculated from complementary tri-stimulus data. It is pointed out that this approach is applicable to the study and evaluation of similar equilibria. From complementary tri-stimulus data for an acid-base indicator and for a screening dye (or dyes) and the calculated indicator constant, the composition of a satisfactorily screened indicator stock solution can be calculated. Examples are given and derived values are compared with experimental results.

THE screening of indicators is an important approach to improving the detectability of end-points. In the past, the proper ratio of an indicator to the screening dye (or dyes) has always been established by trial and error. In a previous paper,[1] it has been shown that complementary tri-stimulus colorimetry permits the calculation of that ratio when the complementary colour co-ordinates of an indicator and of the screening dyes are known, as well as the optical concentration of their stock solutions. In order, for example, to screen the end-point in an acid-base titration at a certain pH value, a solution containing the necessary amount of indicator is brought to that pH value, the absorbance curve is determined, and the complementary colour parameters are calculated.[1]

As will be shown in the present paper, the screening conditions at any pH value within the transition interval of a particular pH indicator can be calculated when the indicator constant and the complementary colour parameters of the indicator in both the acid and base form are known. Further, the indicator constant itself can be calculated from complementary colour parameters.

Determination of indicator constants

From the formula for the dissociation constant of an indicator acid, HI,

$$K_a = K_{in} = \frac{[H^+][I^-]}{[HI]}, \tag{1}$$

the following equation can readily be derived where q is the mole fraction of the indicator in the acid form

$$K_{in} = [H^+] \cdot \frac{1 - q}{q}. \tag{2}$$

By bringing equation (2) into the form of its negative logarithm, thus allowing the introduction of the parameters pK_{in} and pH, the following is obtained

$$pK_{in} = pH - \log\left(\frac{1}{q} - 1\right). \tag{3}$$

This equation holds not only for indicator acids but also for indicator bases, as can be shown by applying the usual definition for the indicator constant of an indicator base, $K_{in} = K_b/k_W$, where K_b is the dissociation constant of the indicator base and k_W is the ionic product of water.

In the first paper of this series[2] it was shown that the mole fraction of a binary mixture of colorants can readily be calculated from complementary colour parameters. In general, the following equation may be used

$$Q_{r,in} = \frac{qQ_{r,m}E_a + (1-q)Q_{r,b}E_b}{qE_a + (1-q)E_b}, \tag{4}$$

where Q_r, are the co-ordinates of the complementary colour point (being represented by u, v, and w for $r = 1$, 2, and 3 respectively). E is the overall absorptivity, and the subscripts m, a and b apply to the colorant mixture, and to substances a and b, respectively. In the present case a and b may be assigned, respectively, to the acid and base form of the indicator.

It should be pointed out, however, that the treatment given here for an indicator can be applied equally well to any analogous dissociation equilibrium involving coloured components. Further, it should be recognised that the concept "colour" is used in the broadest sense, since wavelengths may be selected outside the visible region of the spectrum if relation to the human eye need not be maintained. This was demonstrated in the first paper of this series.[2]

By arrangements of terms, equation (4) may be solved for q.

$$q = \frac{E_b(Q_{r,b} - Q_{r,m})}{E_a(Q_a(Q_{r,m} - Q_{r,a}) + E_b(Q_{r,b} - Q_{r,m})}. \tag{5}$$

By taking the reciprocal of equation (5), separating the fraction, and transposing, the following equation is obtained:

$$\frac{1}{q} - 1 = \frac{E_a}{E_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}}. \tag{6}$$

The left side of this equation is exactly the argument of the logarithmic term of equation (3), and its equivalent may be introduced into equation (3) to yield

$$pK_{in} = pH - \log\left(\frac{E_a}{E_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}}\right). \tag{7}$$

This equation indicates clearly that for the calculation of the indicator constant, only the absorbance curves of the two limiting acid and base forms of the indicators for a transition, and of a mixture of these forms (*i.e.*, at a pH in the transition interval), need be known. From these three curves all the necessary complementary colour parameters can be calculated in the manner previously reported.[1,2]

In order to calculate the E values, the analytical concentration of the indicator

must be known. However, for the pure acid form and the pure base form of a particular indicator solution, the molar concentration is generally the same. Employing the definition

$$J = CEl, \tag{8}$$

where C represents the molar concentration, J the optical concentration and l the length of the light path through the solution, it follows that

$$pK_{in} = pH - \log\left(\frac{J_a}{J_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}}\right). \tag{9}$$

The application of this approach and of equation (9) can be best appreciated through a practical example, namely, the determination of the indicator constant of tetrabromophenolphthalein. In Fig. 1 are shown the absorbance curves of this indicator as the base form, the acid form, and somewhere in the transition interval (actually at pH = 3·75). The concentration of the indicator was not determined and

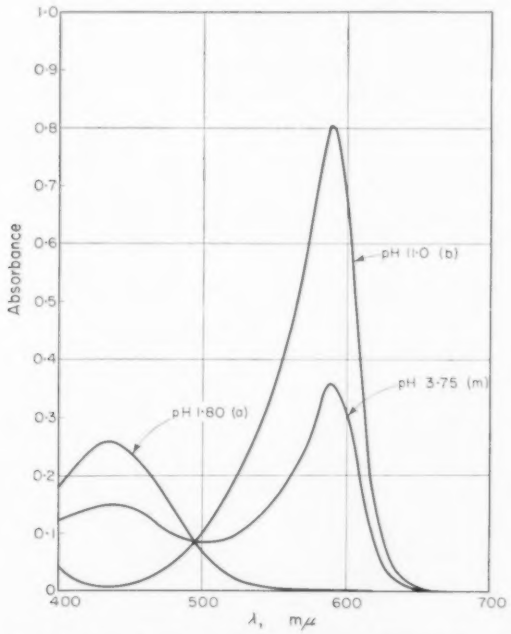

FIG. 1.—Absorbance curves of tetrabromophenolphthalein at various pH values (1-cm cell).

the solution was made up in such a way that reasonable absorbance values would result. By employing the ten selected ordinate method and the mode of calculation previously described,[1] (*i.e.*, with reference to the human eye), the complementary colour parameters for the three colorants given in Table I were obtained.

Formula (9) is actually equivalent to three equations in which Q_r becomes successively u, v, and w for $r = 1, 2$ and 3. Inspection of this equation reveals that differences of the particular co-ordinates are involved. Hence, the form of this equation should be employed for which the greatest numerical differences will result; in this way the

highest accuracy can be secured. The w co-ordinate was selected for the present example in this way. By substituting in equation (9), the result is

$$pK_{in} = 3{\cdot}75 - \log\left(\frac{0{\cdot}227}{0{\cdot}539} \times \frac{0{\cdot}303 - 0{\cdot}794}{0{\cdot}046 - 0{\cdot}303}\right) = 3{\cdot}8_3.$$

The value for $pK_{in} = 3{\cdot}8_3$, thus obtained, is in good agreement with the value, 3·8, accepted in the literature.[3]

Although in this example the ten selected ordinate method was used, it should be emphasised that reference to the human eye is unnecessary, because the value of the

TABLE I.—COMPLEMENTARY COLOUR PARAMETERS FOR TETRABROMOPHENOLPHTHALEIN

	u	v	w	J
Acid form	0·152	0·053	0·794	0·227
Base form	0·462	0·492	0·046	0·539
Mixture, pH 3·75	0·356	0·341	0·303	0·367

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indicator constant is unrelated to the observer's vision. Any suitable number of wavelengths (even one wavelength only in each range) could have been selected appropriately in the visible or non-visible portion of the spectrum.

In exactly the same manner pK_{in} for methyl orange and for cresol red were determined. The respective values, $3{\cdot}4_6$ and $8{\cdot}1_4$, are in good agreement with the values 3·5 and 8·1 accepted in the literature.[3] Multi-step indicator equilibria (or any other analogous dissociation equilibria) can be treated in the same manner, provided that the constants for each step are sufficiently different in magnitude to allow neglect of other steps in the consideration of a single step. Thus, for a pH indicator such as thymol blue, which has two transition intervals, both indicator constants can be calculated, but five absorbance curves are needed: one of the form existing in strongly acidic medium; one in the first transition interval; one of the intermediate form; one in the second transition interval, and one of the form present in strongly alkaline solution. Then equation (9) is applied twice, taking into consideration that in the calculations the intermediate form represents the base form in relation to the first indicator constant, and the acid form in relation to the second indicator constant.

Employing the ten selected ordinate method, the values of $pK_{in,2}$ was found to be $8{\cdot}9_2$ which is in excellent agreement with the value 8·9 reported in the literature for thymol blue[3]. However, the value for $pK_{in,1}$ thus obtained differed considerably from accepted values. The obvious reason for this discrepancy was that the solution with the lowest pH (0·8) measured was not sufficiently acid to ensure the exclusive presence of the acid form. Instead of measuring the absorbance curve of an even more acidic solution, the possibility of calculating the complementary colour parameters for this form without ensuring its exclusive presence was investigated. It was found that this could be accomplished as described below.

Assume that the base form (*i.e.*, the intermediate form in the present case of thymol blue) is obtainable and that its complementary colour parameters have been determined; and further, that the absorption spectrum of the mixed acid-base system is known at two different pH-values in the transition interval. Then, since the indicator

constant is indeed constant, the following relation exists

$$pH_1 - \log\frac{J_a}{J_b} \times \frac{Q_{r,m,1} - Q_{r,a}}{Q_{r,b} - Q_{r,m,1}} = pH_2 - \log\frac{J_a}{J_b} \times \frac{Q_{r,m,2} - Q_{r,a}}{Q_{r,b} - Q_{r,m,2}}, \qquad (10)$$

where the subscripts 1 and 2 refer to the parameter of the system at the two different pH values. Equation (10) can be solved for the unknown complementary colour co-ordinates of the acid form, $Q_{r,a}$, to yield

$$Q_{r,a} = \frac{(Q_{r,b} - Q_{r,m,2})Q_{r,m,1} - \frac{[H^+]_2}{[H^+]_1} \times (Q_{r,b} - Q_{r,m,1})Q_{r,m,2}}{(Q_{r,b} - Q_{r,m,2}) - \frac{[H^+]_2}{[H^+]_1}(Q_{r,b} - Q_{r,m,1})}. \qquad (11)$$

Thus the numerical values of the complementary colour co-ordinates of the acid form can be secured even though they were not directly available by experimentation. These co-ordinates can now be employed to calculate the optical concentration of the acid form, J_a, in the following manner. The argument of the logarithm in equation (9) is equal to $(1/q - 1)$. Further, q can be calculated from the following equation

$$J_m = qJ_a + (1 - q)J_b, \qquad (12)$$

where J_m is the optical concentration of the mixed form (at either of the two pH values). From equation (12) an expression for $(1/q - 1)$ can be derived, namely

$$\frac{1}{q} - 1 = \frac{J_a - J_m}{J_m - J_b}. \qquad (13)$$

This equation may be combined with equation (6), with the E values replaced by the J values according to equation (8), to yield

$$\frac{J_a}{J_b} \times \frac{Q_{r,m} - Q_{r,a}}{Q_{r,b} - Q_{r,m}} = \frac{J_a - J_m}{J_m - J_b}. \qquad (14)$$

From this equation by solving for J_a, the following is obtained

$$J_a = J_b \times J_m \frac{Q_{r,m} - Q_{r,b}}{J_m(Q_{r,m} - Q_{r,a}) - J_b(Q_{r,b} - Q_{r,a})}. \qquad (15)$$

The reliability of this derivation was established by its application to the determination of the complementary colour parameters of the intermediate (yellow) form of thymol blue, which can readily be obtained from experimental data. The necessary data are given in Table II. Since the study is not related to the human eye, the ten selected

TABLE II.—COMPLEMENTARY COLORIMETRIC PARAMETERS OF THYMOL BLUE IN ITS YELLOW AND BLUE FORM AND THEIR MIXTURES

	u	J
Strong base	0·105	4·12
Acid (pH 5)	0·572	4·07
Mixture pH 8·0	0·526	4·08
pH 9·0	0·332	4·10
pH 7·5	0·555	4·07
pH 9·5	0·225	4·10

ordinate method was not mandatory and a simpler selection of wavelength values was made; namely, *u*-range: 410, 420, 430, 440 and 450 mμ; *v*-range: 460, 470, 480, 490 and 500 mμ; *w*-range: 520, 530, 540, 550 and 560 mμ. The values of u_a calculated were 0·579 and 0·575, selecting the pH values of the pairs 7·5 and 9·5; and 8·0 and 9·0, respectively. These values and especially their average, 0·572, compare very favourably with the value obtained directly from the experimental data in Table II, namely, 0·572.

J_a was then calculated by equation (15), employing the two pairs of pH values. The values thus obtained, namely 4·06, and $4{\cdot}07_6$, and their average, 4·07, are in agreement with the experimental value obtained directly, 4·07.

Since the quotients of differences are involved in all of these calculations, small experimental errors can cause considerable deviations. It is therefore desirable to calculate the values from several sets of curves and then to average the results.

When such an amount of calculation and measurement is involved it would obviously be much simpler to run one single curve at the desired pH value and to obtain the results directly from that curve. The simple indicator equilibrium, however, is treated as an instructive example and the procedure derived may advantageously be applied to the study of cases where overlapping equilibria prevent the direct determination of the complementary colorimetric parameters of one particular form.

With this conformation of the derivation at hand, the complementary colour parameters of the form of thymol blue existing in strongly acidic medium were calculated with the intermediate yellow form considered as the base form. Then the absorption spectra of solutions of thymol blue at pH 1·0 and 2·0, and at 1·5 and 2·5, were obtained. The same wavelengths were utilised as in the above consideration of the intermediate form. The u_a value thus obtained for the two pairs of pH values were 0·137 and 0·137, and these were applied to the calculation of J_a. The values secured were, respectively, 7·54 and 7·41. The average of these two values, 7·47, was then used to calculate the indicator constant using *m*-values from the curves at pH 1·0, 1·5 and 2·0. The values of $pK_{in.1}$ obtained, namely, 1·55, 1·59 and 1·56, and their average, $1{\cdot}5_7$ are in good agreement with the value 1·6 accepted in the literature.[3]

Methyl red presents an interesting case, as it has two acid forms which to the eye are almost the same shade of red. As can be seen from Fig. 2, the absorbance curves of these two forms are rather similar and the differences occur in a wavelength range in which the eye is not especially sensitive. By selecting an appropriate number of absorbance curves to cover the pH region, it is possible to calculate the indicator constant for the transition between the two forms. It should be appreciated that knowledge of these indicator constants is of little or no significance in the usual application of methyl red as an acid-base indicator; however, knowledge of the complementary colour parameters is necessary in order to calculate the exact screening condition for this indicator. These parameters were calculated in the same manner as described above and were then used to secure the values of the indicator constants. The average value of $pK_{in.2}$ (single values 4·88, 5·00 and 4·98) was found to be $4{\cdot}9_3$ which is in agreement with the value 4·9 in the literature.[3] The value of $pK_{in.2}$ was found to be 2·3; the same value is recorded in the literature.[4]

When the manuscript of the present paper was in preparation a paper by Reilley and Smith[5] was published. The authors devoted a part of the paper to the determination of indicator constants. Using a somewhat different approach they obtained the

constants through a graphical procedure. Incidentally, they also determined the value of $pK_{in,1}$ for methyl red and reported the values 2·3.

Complementary tri-stimulus colorimetry in the study of equilibria

The appropriate plotting of results derived by complementary tri-stimulus colorimetry offers an excellent tool for the study of equilibria involving colorants. If, as with an acid-base indicator, a simple equilibrium is involved, one component disappears and another appears. In such a case a $u-v$, $u-w$ or $v-w$ plot will yield a straight

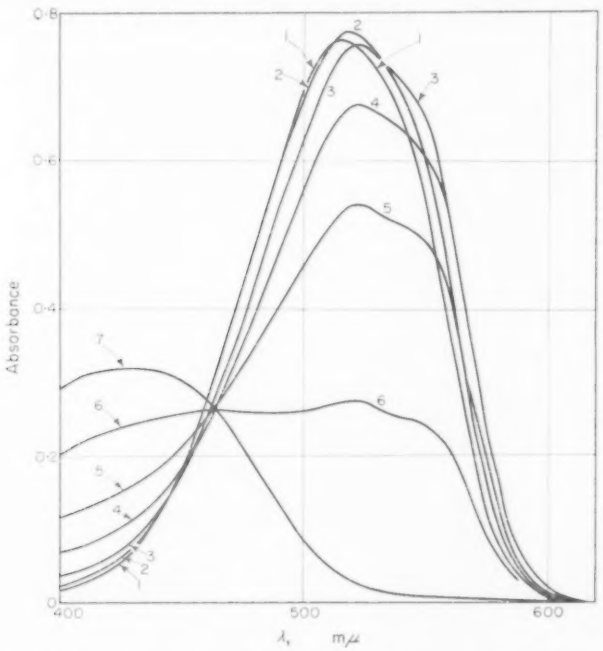

FIG. 2.—Absorbance curves of methyl red at various pH values (1-cm cell).

line. The theoretical background and mathematical derivations have previously been given.[1,2] Such a plot for thymol blue is given in Fig. 3. From point "*a*", denoting the complementary colour point of the indicator form existing in a strongly acidic medium, a straight line passes to point "*i*", corresponding to the intermediate (yellow) form that exists over a wide pH range. With a further increase in pH, the system is represented by a straight line connecting point "*i*" with point "*b*", which corresponds to the form existing in strongly alkaline medium. The calibration of the system lines in pH-units does not result in an equally spaced argument; rather there is "crowding" toward the points "*a*", "*i*" and "*b*". The diagram shown in Fig. 3 can be better appreciated by comparison with the plot shown in Fig. 4.

It is important to appreciate that a pH-Q_r plot (such as in Fig. 4) will not of necessity disclose the occurrence of a multi-step equilibrium. This is illustrated by Fig. 5, which pertains to methyl red. Neither the *u*- nor the *v*-curve reveals that a second equilibrium is operative.

In both curves, the deviations in the region pH 1–4 may be attributed to experimental errors. The *w*-curve, however, shows clearly the presence of a second equilibrium. This can be readily understood by a study of the spectral curves (see Fig. 2);

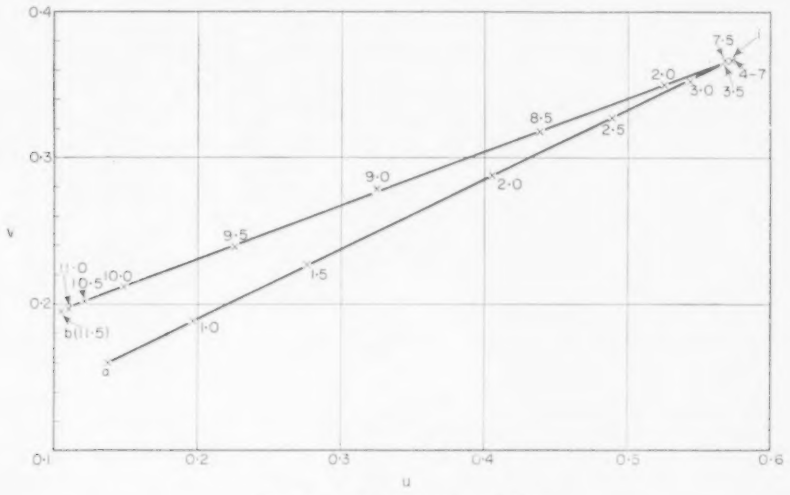

FIG. 3.—*u–v* Plot for thymol blue.
Numbers along the lines are the pH values corresponding to the indicated points; *a* represents the acid form, *i* the intermediate (yellow) form, and *b* the base form.

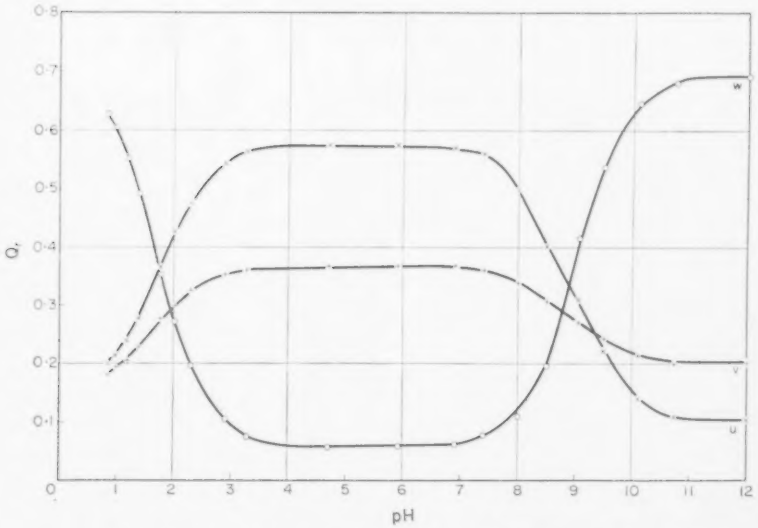

FIG. 4.—Relation of the values of *u*, *v* and *w* to pH for thymol blue.

the changes predominate only in the wavelength region selected as the *w*-range. The two steps of the equilibria are immediately apparent from a *u*—*w* plot as shown in Fig. 6. There is an important association between the existence of a straight line in a *u*—*v* plot and the presence of an isobestic point in the absorbance curves. Both are necessary, but insufficient, conditions for a simple equilibrium.

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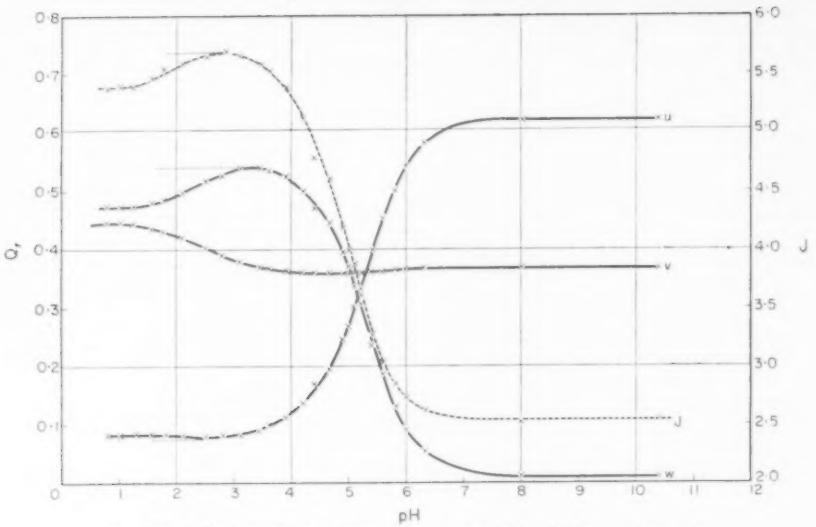

FIG. 5.—Relation of the values of u, v, w and J to pH for methyl red.

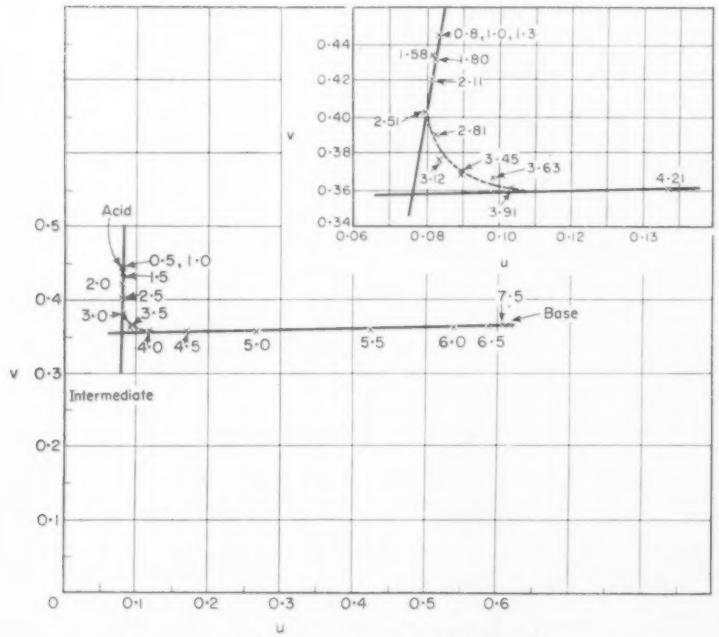

FIG. 6.—u–v Plot for methyl red.
Numbers along the lines are the pH values corresponding to the indicated points. The portion of the system in the vicinity of the colour point of the intermediate form is shown enlarged as an insert.

From this point of view, a closer inspection of the system lines around the intermediate form of methyl red does reveal a curvature (see insert in Fig. 6). To date, the present author has been unable to explain this curvature. It may be caused by some impurity which exhibits indicator properties. Hence the value for pK_1 obtained is somewhat uncertain and the problem needs further investigation.

Calculation of screening conditions

The equations derived in this paper may be applied inversely to the calculation of the complementary colour co-ordinates for any indicator colour in the transition interval, when the indicator constant and the complementary colour co-ordinates of the two limiting forms of that particular transition range are known. Then the screening conditions can readily be calculated for any desired pH in the transition interval. For this particular calculation, of course, not any ordinates may be selected; rather, since reference to the eye is maintained, the ordinates must be selected according to the colour theory. The approach can be readily explained in terms of a practical example, namely, the screening of the acid-base indicator methyl orange at pH 4·08. (This particular value was selected because an absorbance curve was available for it, thus permitting comparison of calculated and experimental results). The concentrations of the indicator and of the screening dye (or dyes) in the screened solution can be calculated from the following equation, which was derived in a previous paper:[1]

$$\sum_{i}^{n} (Q_{r,i} - G_r)J_i = 0. \tag{16}$$

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In this equation G_r represents the complementary colour co-ordinates of the grey point, that is, the complementary colour point obtained for the illuminant alone with no colorants present. The corresponding values for illuminant *C* (representing average day-light) are $u = 0{\cdot}310$, $v = 0{\cdot}316$ and $w = 0{\cdot}374$. Equation (16) is actually equivalent to three equations with $r = 1$, 2, and 3 for u, v and w respectively. Since only two unknowns are involved if two screening dyes are employed (the unknowns are the dye concentrations), only two equations need be considered. These two equations may be written explicitly as follows

$$(u_e - 0{\cdot}310)J_e + (u_{bl} - 0{\cdot}310)J_{bl} + (u_v - 0{\cdot}310)J_v = 0, \tag{17}$$

and

$$(v_e - 0{\cdot}316)J_e + (v_{bl} - 0{\cdot}316)J_{bl} + (v_v - 0{\cdot}316)J_v = 0, \tag{18}$$

where the subscripts *e*, *bl* and *v* refer, respectively, to the end-point colour, and the blue and violet screening dyes. These equations can be simplified for further manipulation by introducing the following definitions

$$(u - 0{\cdot}310) = \bar{u}, \tag{19}$$

and

$$(v - 0{\cdot}316) = \bar{v}. \tag{20}$$

This operation represents a shift of the origin of the co-ordinate system from $u = 0$, $v = 0$ to the grey point. Applying this transformation to equations (17) and (18), the following equations are obtained

$$\bar{u}_e J_e + \bar{u}_{bl} J_{bl} + \bar{u}_v J_v = 0, \tag{21}$$

and

$$\bar{v}_e J_e + \bar{v}_{bl} J_{bl} + \bar{v}_v J_v = 0. \tag{22}$$

What has to be found is in essence the ratio of the volumes of the three solutions, namely of the indicator and of the two screening dyes, which must be mixed in order to secure screening at the selected pH. This can be done by introducing the concept "optical millimoles" and "optical molarity". (One could even speak of the "*J*-ity" of a colorant solution, thus paralleling the molarity.) Then the following equation may be written:

$$ml' \times J' = (J \times ml) \text{ screened solution}, \tag{23}$$

where J' stands for the optical molarity of the stock solution of the three colorants and ml' stands for their volume in millilitres. Equations (21) and (22) can then be written in the following forms:

$$\frac{\bar{u}_e J_e' ml_e'}{ml_e} + \frac{\bar{u}_{bl} J_{bl}' ml_{bl}'}{ml_{bl}} + \frac{\bar{u}_v J_v' ml_v'}{ml_v} = 0, \tag{24}$$

and

$$\frac{\bar{v}_e J_e' ml_e'}{ml_e} + \frac{\bar{v}_{bl} J_{bl}' ml_{bl}'}{ml_{bl}} + \frac{\bar{v}_v J_v' ml_v'}{ml_v} = 0. \tag{25}$$

Of course the volume of the screened solution is the same for all three components; hence, $ml_e = ml_{bl} = ml_v = ml$. This term, which factors out, vanishes because the resulting product equals zero. Then the final result is

$$\bar{u}_e J_e' ml_e' + \bar{u}_{bl} J_{bl}' ml_{bl}' + \bar{u}_v J_v' ml_v' = 0, \tag{26}$$

and

$$\bar{v}_e J_e' ml_e' + \bar{v}_{bl} J_{bl}' ml_{bl}' + \bar{v}_v J_v' ml_v' = 0. \tag{27}$$

In these equations $\bar{u}_e'\bar{v}_e$ and J_e' can be calculated from the corresponding data for the limiting forms of the acid-base indicator, and $\bar{u}_{bl}$, $\bar{v}_{bl}$, $\bar{u}_v$, $\bar{v}_v$, J_{bl}' and J_v' are known from the absorbance curves of the stock solution of the screening dyes.

It is now possible to make ml_e' unity and to solve for the two unknowns ml_{bl}' and ml_v'. This then gives the number of millilitres of each of the stock solutions of the screening dyes which must be mixed with 1 ml of the indicator stock solution in order that the mixture will exhibit grey at the selected pH value.

Solution of the equations is best accomplished by employing determinants and applying Cramer's rule. The result is

$$ml_e' : ml_{bl}' : ml_v' = 1 : \frac{J_e'}{J_{bl}'} A : \frac{J_e'}{J_v'} B, \tag{28}$$

where

$$A = \frac{\begin{vmatrix} \bar{u}_v & \bar{u}_e \\ \bar{v}_v & \bar{v}_e \end{vmatrix}}{\begin{vmatrix} \bar{u}_{bl} & \bar{u}_v \\ \bar{v}_{bl} & v_e \end{vmatrix}}, \tag{29}$$

and

$$B = \frac{\begin{vmatrix} \bar{u}_e & \bar{u}_v \\ \bar{v}_e & \bar{v}_v \end{vmatrix}}{\begin{vmatrix} \bar{u}_{bl} & \bar{u}_e \\ \bar{v}_{bl} & \bar{v}_e \end{vmatrix}}. \tag{30}$$

By applying equation (3) to methyl orange at pH 4·08, the q value can be calculated and is found to be 0·193. Then by applying either equation (4) or (6), and replacing the E values by the J values according to equation (8), the complementary colour co-ordinates $\bar{u}$ and $\bar{v}$ for the end point colour are obtained. Finally J for the end-point colour, that is at pH 4·08, is obtained by application of equation (12). It can be proved very simply that in the latter calculation the Q_r values can be taken instead of the $\overline{Q_r}$ values.

These values and the corresponding values for the two screening dyes are collected in Table III, which also contains the results obtained from the spectral curve for methyl orange at pH 4·08. Application of equations (28), (29) and (30) established

TABLE III.—COMPLEMENTARY COLORIMETRIC PARAMETERS FOR CALCULATING THE SCREENING CONDITIONS OF METHYL ORANGE

	$\bar{u}$	$\bar{v}$	J
Indicator acid form	−0·177	0·055	28·29
base form	−0·173	−0·214	21·83
pH 4·00 calculated	−0·174	−0·150	23·08
pH 4·08 experimental	−0·173	−0·152	23·26
Screening dye Blue CI 671	0·274	0·081	16·61
Violet CI 697	0·071	0·246	24·35

that the volumes of the violet and blue screening dye solutions to be added to one millilitre of indicator stock solution were, respectively, 0·509 and 0·888 ml. The three solutions were then mixed in these indicated proportions and several drops of the resulting solution were added to a dilute hydrochloric acid solution. An aliquot of this solution was then titrated with sodium hydroxide solution by three different persons in average daylight to the grey point. The pH values of the titrated solutions were measured and were found to be 4·00, 4·02 and 4·06. The agreement is excellent

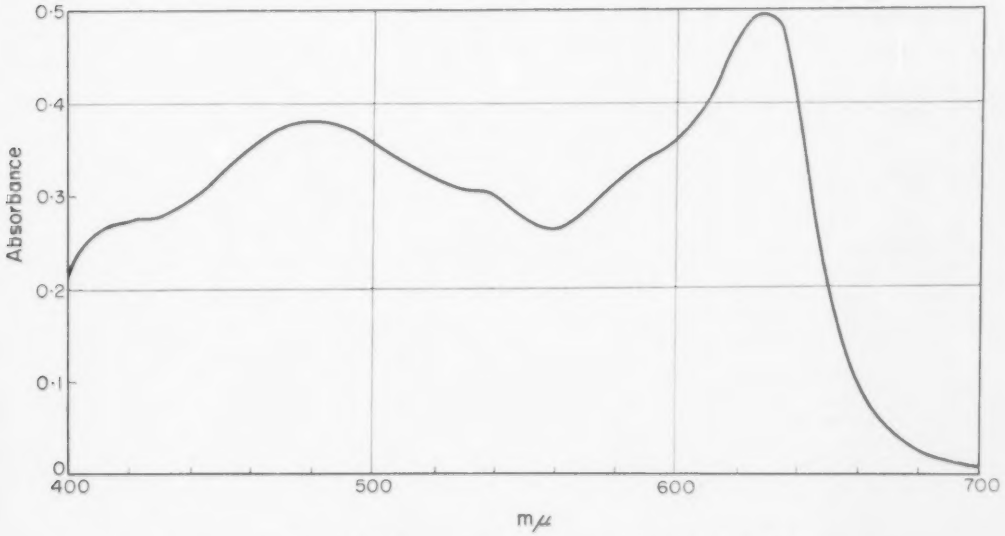

FIG. 7.—Absorbance curve of the screened methyl orange indicator at pH 4·08 (5-cm cell).

when it is recognised that none of the observers possesses the hypothetical "average" eye and that the illuminant did not exactly correspond to standard illuminant *C*. Fig. 7 shows the absorbance curve for the screened indicator at appropriate dilution and brought to exactly pH 4·08. The $\bar{u}$ and $\bar{v}$ values of that curve are 0·313 and 0·314, which within experimental error corresponds to the actual co-ordinates of the grey point, that is, 0·310 and 0·316, respectively.

When a similar approach was applied to the screening of tetrabromophenolphthalein good agreement was also obtained. In this case, however, it proved to be advisable to use a rather low concentration of the indicator in the solution to be actually titrated and to observe the end-point colour change through a short light path. The screened indicator mixture exhibits dichromatism to a higher degree than the pure indicator. This observation was also made with some other systems, and further studies are being made of this phenomenon. Probably such difficulties can be overcome by appropriate selection of the screening dyes.

EXPERIMENTAL

All reagents used were of analytical grade except the screening dyes which were applied as obtained from the manufacturer. The absorbance curves of the indicators were obtained in the following manner: A stock solution of the indicator was prepared in either water or alcohol, as appropriate. Then a known volume of this stock solution was transferred to a volumetric flask and diluted to the mark with 0·1*N* hydrochloric acid. A second identical aliquot of the stock solution was transferred to a second volumetric flask (of the same volume as the first) and diluted to the mark with 0·1*N* sodium hydroxide. Some of the acidic indicator solution was transferred to a beaker and titrated with the basic solution. The pH values were measured with a Beckman pH meter and portions of the solution having the appropriate pH values were transferred to cuvettes and their absorbance curves measured by use of a Cary model 14 recording spectrophotometer. Absorbance and pH measurements were made at room temperature 25 ± 2°.

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Zusammenfassung—Es wird gezeigt, dass die Indikatorkonstanten von Säure-Basenindikatoren mittels komplementärer Tristimulusdaten errechnet werden können. Es wird hingewiesen, dass diese Art von Berechnungen auch auf ähnliche Gleichgewichte ausgedehnt werden kann. Aus den komplementären Tristimulusparametern für den Indikator und für die zuzumischenden, inerten Farbstoffe, sowie der Indikatorkonstante kann die Zusammensetzung einer Indikatormischung berechnet werden, die bei einem bestimmten pH-Wert ein neutrales Grau zeigt. ("Gescreenter" Indikator).

Résumé—L'auteur montre que les constantes des indicateurs acide-base peuvent être calculées à partir des résultats des tristimuli. Il fait remarquer que cette méthode est applicable à l'étude et à l'évaluation d'équilibres semblables. A partir des résultats des trismuli pour un indicateur acide-base et pour un colorant (ou des colorants) "protecteur" et de la constante calculée de l'indicateur, la composition d'une solution stable d'indicateur "protégé" de façon satisfaisante peut être calculée. Des exemples sont donnés et des valeurs dérivées sont comparées avec les résultats expérimentaux.

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SELECTION OF COMPLEXING AGENTS FOR COMPLEXOMETRIC TITRATIONS*

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Summary—It is shown how conditional (*i.e.*, apparent) constants can be used to choose the most suitable complexing agent for the titration of a metal in the presence of other metals. The titration of barium is considered as an example. This titration can be performed with satisfactory accuracy with DTPA or EGTA, employing indirect end-point detection. Curves plotting the theoretical titration errors of the titrations are presented.

Calcium can be determined in the presence of magnesium with EGTA, using Zincon and zinc-EGTA for indirect end-point detection. The theoretical titration error has been evaluated for titrations under various experimental conditions.

ETHYLENEDIAMINETETRA-ACETIC acid (EDTA) holds a special position as a titrant in complexometric titrations, but frequently better results can be obtained in titrations if another polyamino-polycarboxylic acid is substituted for it. In recent years the applicability of several polyamino-polycarboxylic acids as complex-forming titrants has been studied, and in this paper two of these acids, diethylenetriaminepenta-acetic acid (DTPA), and ethyleneglycol-bis-(aminoethylether)tetra-acetic acid (EGTA), will be compared with ethylenediaminetetra-acetic acid to determine whether they are more suitable titrants than EDTA itself.

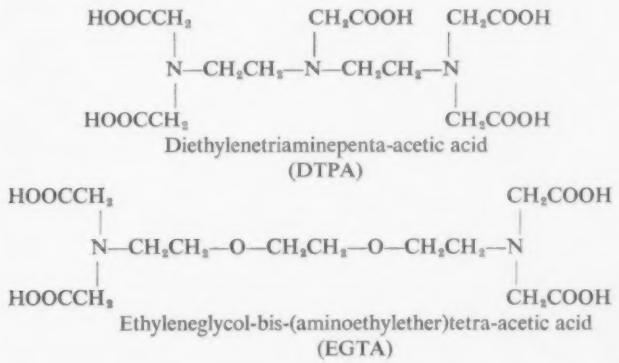

FIG. 1.

The structures of the two new acids are shown in Fig. 1. The complexing properties of these acids can be compared with those of EDTA by choosing a suitable reference metal.

The comparison can be made most simply by plotting the values of the *conditional*

* A paper read at the 10:e Nordiska Kemistmötet, Stockholm, 1959.

*constants** of the complexes formed by this metal with the three acids as functions of pH. The conditional constant of a 1:1 complex MY, formed by the metal M and the complexing agent H_nY, is computed from the equation:

$$K_{M'Y'} = [MY]/([M'][Y']) = K_{MY}/(\alpha_M \alpha_Y), \tag{1}$$

where K_{MY} is the stability constant of the complex at the ionic strength in question and α_M and α_Y are so-called side-reaction coefficients[2] defined by

$$\alpha_M = [M']/[M], \tag{2}$$

$$\alpha_Y = [Y']/[Y]. \tag{3}$$

[M'] denotes the concentration of the metal ion and [Y'] the concentration of the complexing agent (ligand) that has *not* reacted to form the complex MY, irrespective of the form in which each exists in the solution. In an ammoniacal solution, for example, the metal ion may form several complexes with ammonia, and then

$$[M'] = [M] + [M(NH_3)] + [M(NH_3)_2] + \ldots + [M(NH_3)_p]. \tag{4}$$

Similarly, if no interfering cations other than the hydrogen ion are present, we may write

$$[Y'] = [Y] + [HY] + [H_2Y] + \ldots + [H_nY]. \tag{5}$$

The numerical values of the side-reaction coefficients are calculated with the aid of the equations:

$$\alpha_{M(L)} = 1 + \sum_{p=1}^{p} [L]^p K^M_{ML_p}; \qquad K^M_{ML_p} = [ML_p]/([M][L]^p), \tag{6}$$

and

$$\alpha_{Y(N)} = 1 + \sum_{q=1}^{q} [N]^q K^Y_{N_qY}; \qquad K^Y_{N_qY} = [N_qY]/([N]^q[Y]), \tag{7}$$

in which L denotes an interfering ligand (an anion, which may be the hydroxyl ion, or a molecule) and N denotes an interfering cation (also the hydrogen ion).

If N in equation (7) represents the hydrogen ion, $K^Y_{N_qY}$ is the over-all proton stability constant defined by the equation

$$K^Y_{N_qY} = K^Y_{H_nY} = [H_nY]/([H]^n[Y]). \tag{8}$$

For the comparison of the properties of the complexing agents we present the values of the conditional constants of the barium complexes of the acids. Because the barium ion does not form complexes with the hydroxyl ion or ammonia, α_{Ba} is equal to unity and the value of the conditional constant varies inversely as $\alpha_{Y(H)}$. The variation of the conditional constants of the different barium complexes is shown by the curves in Fig. 2.

The possible formation of binuclear barium complexes of DTPA,[5] which would cause the value of α_{Ba} to deviate from unity, has not been taken into account when computing the values of the conditional constant of the barium-DTPA complex, but this formation cannot be expected to have any appreciable influence on the calculated curve.

* The term "conditional constant", which corresponds to "apparent constant" employed by Schwarzenbach,[1] was introduced by Kolthoff and Ringbom.[2,3] Reilley[4] has used the name "effective constant" for the same purpose.

It will be seen from Fig. 2 that DTPA and EGTA are the best complexing agents for the titration of barium at pH 10. For direct end-point detection the indicator Metalphthalein[6] could be employed, but owing to the tendency of the indicator to form coloured acid and binuclear complexes, its use requires a very accurate adjustment of the pH of the solution (to pH $\simeq$ 11·5). Other means of end-point detection have been proposed. Thus Schwarzenbach[1] has suggested the use of Eriochrome Black T, together with the magnesium or zinc complex of the complexing agent, in the titration of barium with EDTA. The sharpness of the colour change is not, however, quite satisfactory in this case, and therefore it is of interest to determine whether a better end-point detection can be achieved with DTPA or EGTA.

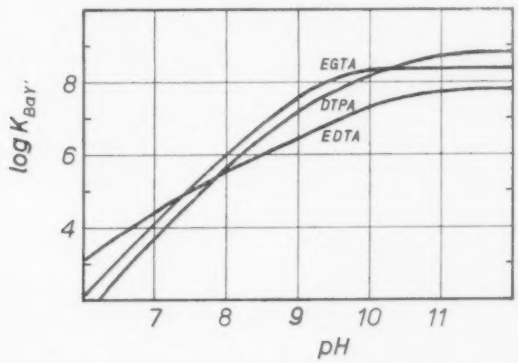

FIG. 2.—Conditional constants of barium complexes as functions of pH.

The Titration of Barium with Indirect End-point Detection

The theoretical treatment of a titration with indirect end-point detection requires a knowledge of the equilibrium conditions of the reactions:

$$M_I + M_{II}Y \rightleftharpoons M_IY + M_{II} \quad (9)$$

$$M_{II} + I \rightleftharpoons M_{II}I. \quad (10)$$

M_I is the metal ion to be determined, Y the complexing agent, M_{II} an added auxiliary metal ion, and I an indicator that changes colour when it reacts with the latter metal ion. When Eriochrome Black T is employed as indicator, the most suitable auxiliary metal ion is magnesium or zinc.

The values of the stability constants of the barium, magnesium and zinc complexes of the three complexing agents under consideration are collected in Table I.

TABLE I.—VALUES OF THE STABILITY CONSTANTS OF THE BARIUM, MAGNESIUM AND ZINC COMPLEXES OF DTPA, EGTA AND EDTA.

	$\log K_{MgY} - \log K_{BaY}$	$\log K_{ZnY} - \log K_{BaY}$
DTPA	9·3 − 8·8 = 0·5	18·0 − 8·8 = 9·2
EDTA	8·7 − 7·8 = 0·9	16·5 − 7·8 = 8·7
EGTA	5·4 − 8·4 = −3·0	12·8 − 8·4 = 4·4

A. *Titration of barium in the presence of the magnesium complex of the complexing agent*

In order that Eriochrome Black T and the magnesium complex of the complexing agent can be employed to indicate the end-point of the titration of barium with another complexing agent, with a greater accuracy than with EDTA as titrant, the difference between the stability constants of the magnesium and barium complexes must be smaller for the former complexing agent than for EDTA. The difference

$$\Delta \log K^{Mg,Ba} = \log K_{MgY} - \log K_{BaY} \qquad (11)$$

is seen to be the smallest for EGTA ($\Delta \log K^{Mg,Ba}_{EGTA} = -3{\cdot}0$), but since the stability constant of the magnesium complex must exceed the value 10^7 before the end-point can be detected visually with sufficient accuracy, DTPA is more suitable for the determination of barium. This has been shown to be the case previously in the analysis of small amounts of barium and, indirectly, of small amounts of sulphate.[7]

The theoretical titration error in such a complexometric titration is given by

$$\text{Titration error} = ([Y'] - [M_I'] - [M_{II}'])/[M_IY]. \qquad (12)$$

When conditional constants are introduced into this equation, we obtain

$$\text{Titration error} = [M_{II}Y]/([M_IY][M_{II}']\,K_{M_{II}'Y'}) - [M_{II}']\,K_{M_I'Y'}/([M_{II}Y]\,K_{M_{II}'Y'}) - [M_{II}']/[M_IY]. \qquad (13)$$

The theoretical titration error in the titration of barium ($= M_I$) with DTPA, in the presence of the magnesium-DTPA ($= M_{II}Y$) complex, is plotted as a function of the concentration of the latter in Fig. 3. At pH 10 Eriochrome Black T turns blue when $[Mg] \leq 10^{-5.9}$ ($pMg \geq 5{\cdot}9$).

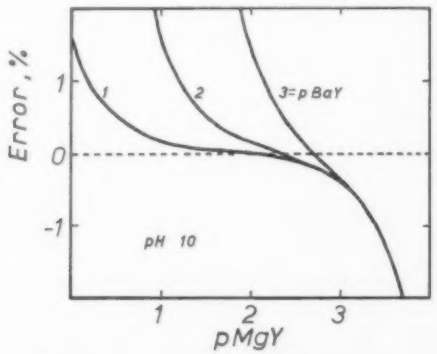

FIG. 3.—Theoretical titration error in the simultaneous titration of barium and magnesium ions with DTPA as a function of the concentration of added magnesium-DTPA complex. pH 10. $pMg_{end\text{-}p.} = 5{\cdot}9$. Indicator : Eriochrome Black T.

From the Figure it is seen that good results can be expected when the magnesium complex is added to a barium salt solution of unknown concentration until its concentration is about $10^{-3}M$. Titration errors[7] found experimentally conform fairly well with the curves shown in Fig. 3.

B. *Titration of barium in the presence of the zinc complex of the complexing agent*

When the zinc complex and Eriochrome Black T are employed for indirect end-point detection in the titration of barium, the difference between the stability constants of the zinc and barium complexes of the new titrant must be smaller than the difference for the corresponding complexes of EDTA. This difference is seen to be smallest for EGTA (Table I), and hence this complexing agent is more suitable than EDTA for the titration of barium.

Eriochrome Black T can be employed, together with the zinc complex of the complexing agent, as an indicator for the indirect end-point detection in the titration of barium, if the conditional constant of the zinc complex is of the same order of magnitude as that of the barium complex. Only when this is the case can the indicator react with the zinc ions that are liberated by reaction (9), and a titration is then possible. The conditional constant of the zinc complex can be diminished by adding another complexing agent that reacts only with the zinc ion. Ammonia is a suitable reagent for this purpose. Values of $\alpha_{Zn(NH_3)}$ computed from equation (6), and the values of the conditional constant ($K_{Zn'I'}$) of the zinc-Eriochrome Black T complex ($\log K_{ZnI} = 12{\cdot}9$) at various ammonia concentrations, are given in Table II. The conditional constant of the zinc-indicator complex is computed from

$$K_{Zn'I'} = K_{ZnI}/(\alpha_{Zn(NH_3)}\alpha_{I(H)}). \qquad (14)$$

TABLE II.—$\alpha_{Zn(NH_3)}$ AND $K_{Zn'I'}$ AS FUNCTIONS OF THE AMMONIA CONCENTRATION AT pH 10.

$-\log [NH_3]$	0	0·5	1·0	1·5	2·0
$\log \alpha_{Zn(NH_3)}$	9·0	7·0	5·0	3·1	1·5
$\log K_{Zn'I'}$	2·3	4·3	6·3	8·2	9·8

The calculations have been based on the stability constants of the zinc ammine complexes given in Bjerrum, Schwarzenbach and Sillèn's[8] compilation.

From Table I it can be seen that the conditional constant for the zinc-EGTA complex should be lowered by 4·4 logarithmic units in order that EGTA's barium- and zinc complexes shall be equally strong, and the corresponding lowering on titration with EDTA ought to be 8·7 units. Table II gives information on the ammonia concentration which the solution should contain in order that the necessary lowering of the conditional constant of the zinc complex shall be attained. In the former case about 0·1*M* ammonia is sufficient, in contrast to the latter, which requires about 1*M* concentration.

At a lower ammonia concentration the value of $\alpha_{Zn(NH_3)}$ will be lower, and the conditional constant of the zinc-indicator complex higher in value. When the conditional constant of the zinc-indicator complex is too low, as in the titration with EDTA ($\log K_{Zn'I'} = 2{\cdot}3$), a visual end-point detection is not possible. This difficulty can, in some degree, be overcome if the zinc-indicator complex reacts with ammonia to form a so-called heterobiligand zinc-ammine-indicator complex. Reilley and Schmid[9] have determined the stability constant of the mixed zinc-ammine complex of the indicator Eriochrome Blue Black R and obtained the value $K^{NH_3}_{NH_3ZnI} = 10^{3{\cdot}9}$

The formation of such a complex increases the conditional constant of the zinc-indicator complex to the value given by

$$K_{Zn'I'(ZnI)'} = \alpha_{ZnI(NH_3)} K_{ZnI} / (\alpha_{Zn(NH_3)} \alpha_{I(H)}) \qquad (15)$$

where

$$\alpha_{ZnI(NH_3)} = 1 + [NH_3]\, K^{NH_3}_{NH_3ZnI} \; ; \quad K^{NH_3}_{NH_3ZnI} = \frac{[NH_3ZnI]}{[ZnI][NH_3]}. \qquad (16)$$

The curves in Fig. 4 plot the theoretical titration error in the titration of barium with EGTA, in the presence of zinc-EGTA, at different ammonia concentrations. The errors have been computed from equation (13).

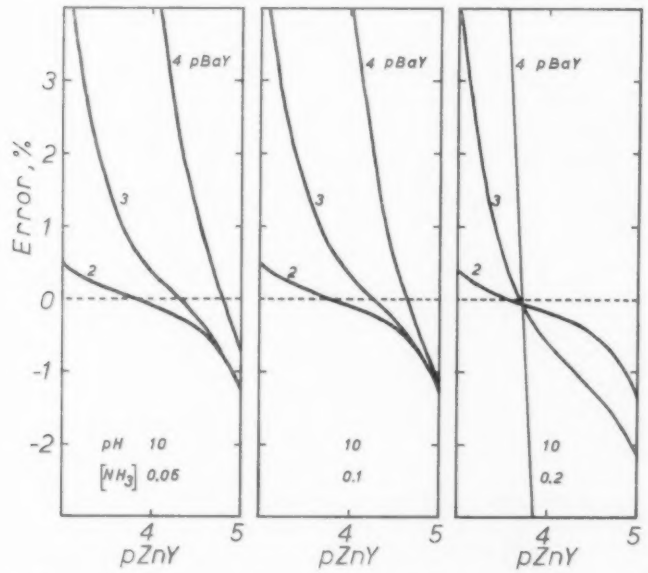

FIG. 4.—Theoretical titration error in the titration of barium with EGTA as a function of the concentration of added zinc-EGTA complex and of the ammonia concentration at pH 10. Indicator: Eriochrome Black T.

Experimentally determined titration errors are in satisfactory agreement with the theoretical errors plotted in Fig. 4, except at high ammonia concentrations, where positive errors are found. This is evidently because of the formation of the zinc-ammine-indicator complex.

The titration employing zinc and EGTA is more accurate than that in which magnesium and DTPA are used.

The titrations of barium with EGTA were performed as follows:

To 10 ml of an approximately 0·01*M* barium chloride solution were added 5 ml of buffer solution (2*M* in ammonia and 0·4*M* in ammonium chloride; pH 10), 5 ml of 0·002*M* zinc-EGTA solution, 0·5 ml of 0·1% alcoholic Eriochrome Black T solution, and the resulting solution was diluted to 80 ml with distilled water. The titration was carried out with 0·0233*M* disodium ethyleneglycol-bis-(aminoethylether)tetra-acetate solution.

The results of a number of titrations conducted in the presence of different ammonia and zinc-complex concentrations are collected in Table III. The colour change

from red to blue was relatively sharp when the ammonia concentration was suitable (0·05–0·1*M*).

TABLE III.—TITRATION OF BARIUM WITH EGTA IN THE PRESENCE OF ZINC-EGTA AND AMMONIA. pH 10.

pZnY	$[NH_3]$	Barium taken, *mmole*	Barium found, *mmole*	Error, %
3·4	0·05	0·0999	0·1004	+0·4
3·7			0·1002	+0·2
4·0			0·1000	+0·1
4·7			0·0962	−3·7[a]
4·0	0·1		0·1004	+0·4
4·0	0·2		0·1030	+3·0[b]
4·0	0·25		0·1055	+5·5[b]

[a] pZnY too high
[b] $[NH_3]$ too high

Titration of Calcium in the Presence of Magnesium

A condition that must be fulfilled before a metal ion M_I can be titrated in the presence of a second metal ion M_{II} is that the difference between the logarithmic conditional constants of the complexes formed by the two metals

$$\Delta \log K^{M_I'M_{II}'} = \log K_{M_I'Y'} - \log K_{M_{II}'Y'} \qquad (17)$$

is sufficiently large (at least four logarithmic units). In addition, as previously mentioned, the conditional constant $K_{M_I'Y'}$ of the complex of the first metal must be larger than 10^7 before a visual titration of the metal ion M_I can succeed.

A titration of calcium in the presence of magnesium is, therefore, not possible with EDTA or DTPA ($\Delta \log K_{EDTA}^{Ca,Mg} = 2{\cdot}0$; $\Delta \log K_{DTPA}^{Ca,Mg} = 1{\cdot}3$), but can be carried out with EGTA because the difference between the logarithmic conditional constants of the EGTA complexes of the two metals is 5·6. A method, based on the use of this complexing agent and an indirect end-point detection, has been proposed by Ringbom, Pensar and Wänninen[10] and later by Sadek, Schmid and Reilley.[11]

The reaction $M_{II} + Y \rightleftharpoons M_{II}Y$ interferes in the determination of M_I and the degree of the interference is determined by the stability constant of the complex $M_{II}Y$ and the concentration of the metal ion M_{II}. Ringbom[2,3] has shown that this reaction can be considered a normal side reaction of the complexing agent which requires the introduction of the side reaction coefficient

$$\alpha_{Y(M_{II})} = ([Y] + [M_{II}Y])/[Y] = 1 + [M_{II}]\, K_{M_{II}Y} \qquad (18)$$

into the expression for the over-all coefficient α_Y, which then becomes

$$\alpha_Y = \alpha_{Y(H)} + \alpha_{Y(M_{II})} - 1 \simeq \alpha_{Y(H)} + \alpha_{Y(M_{II})}. \qquad (19)$$

If the term $\alpha_{Y(M_{II})}$ is the dominating one in (19), and further, if $[M_{II}]\, K_{M_{II}Y} > 1$, the conditional constant of M_IY may, when $\alpha_{M_I} = 1$, be written

$$\log K_{M_IY'} = \Delta \log K^{M_IM_{II}} + pM_{II}. \qquad (20)$$

This equation can be used to evaluate the conditional constant of the calcium

complex of EGTA in the presence of magnesium.[10] Since log $K_{Ca\text{-}EGTA} = 11{\cdot}0$ and log $K_{Mg\text{-}EGTA} = 5{\cdot}4$,

$$\log K_{CaY'} = 5{\cdot}6 + pMg. \tag{21}$$

In the titration, the metal indicator Zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene) and zinc-EGTA can be employed for indirect end-point detection. The stability constant of the zinc-Zincon complex has been evaluated previously.[10]

Because the determination of calcium in the presence of magnesium is an analysis frequently encountered, an estimate of the accuracy attainable in the titration is of particular interest. The theoretical titration error can be computed with the aid of equation (13). The results of such calculations are shown in Fig. 5.

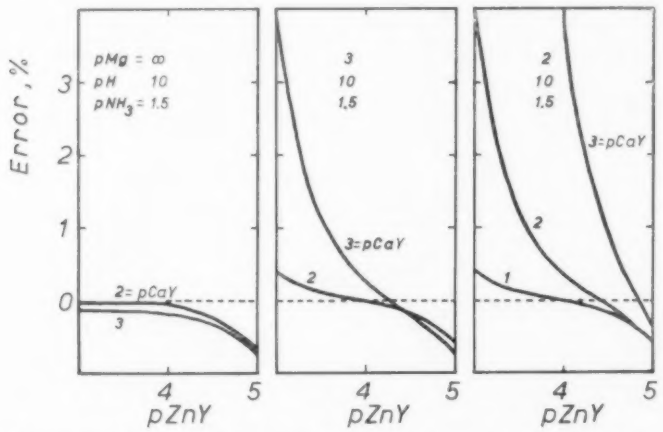

FIG. 5.—Theoretical titration error in the titration of calcium with EGTA at pH 10 in the presence of different concentrations of magnesium ion and zinc-EGTA in solutions containing Zincon and ammonia (0·03 *M*). The colour change takes place when $pZn' = 5{\cdot}9$.[10]

It will be seen from Fig. 5 that the titration error is very low, as long as the concentration of the zinc-EGTA complex does not exceed $10^{-4}M$ and the magnesium ion concentration does not exceed that of the calcium ion.

Acknowledgement—I am indebted to Professor Anders Ringbom for stimulating discussions and comments relating to the manuscript.

Zusammenfassung—Es wird gezeigt, wie man die effektiven (scheinbaren) Stabilitätskonstanten heranziehen kann um das bestgeeignete Komplexbildungsreagen für eine Titration eines Metalles in Gegenwart anderer Metalle zu finden. Die Bestimmung von Barium wird als Beispiel herangezogen. Diese Bestimmung kann mit befriedigender Genauigkeit durchgeführt werden, indem man Diäthylentriaminpentaessigsäure (DTPE) und Äthylenglykol-bis-(aminoäthyläther)-tetraessigsäure (ÄGTE) heranzieht und indirekte Endpunktsanzeige verwendet. Titrationskurven werden gezeigt und der Titrationsfehler berechnet. Calcium kann in Gegenwart von Magnesium mit ÄGTE bestimmt werden wobei Zincon-Zink ÄGTE als Indicatorsystem verwendet wird. Der theoretische Titrationsfehler unter verschiedenen Titrationsbedingungen wurde berechnet.

Résumé—L'auteur montre comment les constantes conditionnelles (c'est-à-dire apparentes) peuvent être utilisées pour choisir l'agent complexant le plus convenable pour le titrage d'un métal en présence d'autres métaux. Le titrage du baryum est pris comme exemple. Il peut être réalisé avec une précision

satisfaisante par l'acide diéthylènetriaminepentacétique (DTPA) et par l'acide éthylèneglycol-bis-(aminoéthyléther) tétracétique (EGTA) en utilisant une détection indirecte du point équivalent. Des courbes montrant les erreurs théoriques de titrage ont été tracées. Le calcium peut être dosé en présence de magnésium par l'EGTA en utilisant le zincon et le complexe zinc-EGTA pour déceler indirectement le point équivalent. L'erreur de titrage théorique a été évaluée pour des titrages dans différentes conditions expérimentales.

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Talanta, 1961, Vol. 8, p. 364. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Reported explosion in the periodic acid Liquid Fire reaction

SIR:

I have read the report, by Mr. J. Thomson, of an explosion due to the use of the Smith and Diehl Periodic Acid Liquid Fire reaction. Like all reactions employing perchloric acid, it would appear that users will take particular pleasure in publicising this—if possible in an hysterical tone of expected explosions. This has been the curse of the promotion of perchloric acid reactions—the aim seems to be to give as big a black eye as possible when a perchloric acid reaction gets out of hand. It makes no difference if such reported explosions are obviously the result of faulty techniques.

The Periodic Acid Liquid Fire Reaction is intended for use in the wet oxidation of organic compositions which are essentially cellulose, protein, sugar and polyhydric alcohols, plastics (excluding polyethylene) or coal. I do not know whether the sample used in this violent reaction reported by Mr. Thomson fell into this category or not. But one thing is as clear as crystal, that the published directions call for the use of 1·5 g of periodic acid per gram of material to be oxidised. Mr. Thomson used a 5-g sample, and added only 3 g of periodic acid, whereas 7·5 g are specified. The principal use of periodic acid is to break down the organic material before the reaction of perchloric acid to complete the oxidation. Obviously if one has insufficient periodic acid present the reaction will not be normal.

Then, too, the reaction is easily stopped if it does not show normal features. All you need to do is to pour 25–30 ml of water down the condenser into the reaction mixture, and no violence is then possible. The exothermic reaction building up is then immediately quenched. Mr. Thomson had plenty of time to do this, as his manipulations prove. This would have enabled him to cogitate at his leisure on what fault there was to be found in his experimental approach, and to adjust reagent amounts as required.

The writer has utilised this reaction type before audiences many times without any protection for the experimenter or for the audience. And no violence was predicted or realised.

Since 1920, perchloric acid has been a name to stampede 99 per cent of the world's chemists. The sale in 1920 was a few hundred pounds annually, world wide. To-day, perchloric acid is utilised in control laboratories in the U.S.A. to the extent of two million pounds annually. The number of routine analytical determinations in the control laboratories of the iron and steel, leather, and agricultural control procedure laboratories amounts to many millions of individual determinations annually. This is in spite of a dozen or more perchlorate explosions that have been reported in the chemical literature. But this reagent continues to increase in consumption. Now that the solid fuel rocket programme is to use 100,000 tons of ammonium perchlorate in 1961 (*Chem. Eng. News*), the popularity of perchlorate oxygen carriers will further enhance the field of perchlorate technology, until even the common textbooks of chemistry will begin to teach the basic principles involved.

It was not good practice to report this mishap without first contacting either of the two authors of the published procedure in question. If Mr. Thomson will be so kind as to send me a sample of the pigment involved in his explosion, I will attempt its wet oxidation in my own laboratory and report the proper procedure to employ. And I am sure that I will not fail to find a suitable reaction mixture.

Very truly yours,

G. FREDERICK SMITH
(Professor of Chemistry, Emeritus.)

William Albert Noyes Laboratory
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois, U.S.A.
16 *February* 1961

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BOOK REVIEWS

The Use of Organic Reagents in Inorganic Analysis. A. I. BUSEV and N. G. POLIANSKII. Translated by J. T. GREAVES. Pp. 76. Pergamon Press Ltd., 1960, 21s.

THIS little book is an English translation of a Russian review article which, apart from a few general references, covers papers published during the years 1953 to 1955 inclusive. The use of organic reagents in chromatography and many applications of complexans in analysis are not included.

There are two chapters in the book; the first rightly deals with general problems in the use and behaviour of organic reagents. The second outlines very briefly what the authors regard as the more important methods of determining the elements using organic reagents.

While the largely uncritical and disjointed presentation of the material is regrettable, there appear to be few mistakes of a technical nature and a good point is the adherence to chemical names rather than the sometimes all too prevalent reliance on trivial names for complicated organic molecules.

In view of the short period of time covered and its limitations in size and scope, the book can hardly be regarded as a major work in this field. It is nevertheless a useful contribution to the literature on organic reagents and it provides English-speaking readers with information (albeit somewhat sketchily and out of date) on developments and trends in this branch of analysis in the Soviet Union.

S. J. LYLE

Chemical Instrumentation. A systematic approach to instrumental analysis. HOWARD A. STROBEL. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960. pp. 653. $9.75.

THE author mentions in his preface, "this text has grown out of the teaching of two one-semester advanced courses in instrumental analysis, one emphasizing optical methods, the other emphasizing electric techniques." After two excellent introductory chapters on the "Science of Instrumentation" and "Errors of Measurement," there follows seven chapters on "Opticometric Methods" and eight chapters on "Electrometric Methods." In the appendix are outlined twenty-four well chosen experiments designed to illustrate the application of the instruments and techniques common to the modern analytical laboratory.

This book is a refreshing departure from the usual loosely organised texts on this subject in that it treats instrumentation as a science in itself built on the foundations of physics, physical chemistry, and engineering. Accordingly, background chapters on the interaction of electromagnetic radiation and matter, physical optics, electrical and electrochemical theory, and electronics are included. These are generally very well written and amply illustrated with well-conceived figures.

In the chapter on the interaction of electromagnetic radiation and matter, the reviewer is gratified to see a short section devoted to optical dispersion, a subject which unfortunately is usually entirely neglected in other books on instrumentation. However, one feels the rest of this chapter is too brief and not up to the high standard of quality set by the remainder of the book.

One small error was noted on page 41 in the legend of Fig. 3–5 which gives the impression that radiative transitions from excited electronic states can occur in 10^{-14} to 10^{-7} sec. A figure of 10^{-9} sec. would be more nearly correct for the minimum time.

EDWIN W. ABRAHAMSON

Chromatographic Reviews. Progress in Chromatography, Electrophoresis and Related Methods. Volume 2. Edited by M. LEDERER. Elsevier Publishing Company, 1960. pp. viii + 195. 46s.

JUST as volume 1 of this compilation contained review articles which were published in the Journal of Chromatography during 1958, the present volume contains reviews which appeared in the Journal during 1959. The six reviews reprinted are:

Review of Gas-Liquid Chromatography (43 pp. 619 references) by C. J. Hardy and F. H. Pollard (Bristol),
Starch Electrophoresis: I. Starch Block Electrophoresis (15 pp. 62 references) by H. Bloemendal (Amsterdam),
Paper Chromatography of Dinitrophenylamino Acids (45 pp. 100 references) by G. Biserte *et al.* (Lille),
The Chromatography of the Flavanoid Pigments (24 pp. 91 references) by J. B. Harborne (Hertford),
The Separation of Different Types of Human Haemoglobin (42 pp. 84 references) by H. K. Prins (Amsterdam), and
Inorganic and Precipitation Chromatography (20 pp. 211 references) by E. Hayek (Innsbruck).

The paper by Biserte *et al.*, originally printed in French, has been translated into English, as has Hayek's review, which first appeared in German.

A critical discussion of six reviews on such widely differing aspects of chromatography is clearly beyond the scope of a single reviewer. Commenting in general terms only, the articles are comprehensive within the limitations of their size and they are sufficiently well referenced to be of value to all workers interested in the topics discussed. The literature coverage is commendably up-to-date, bearing in mind the initial date of publication; but inevitably in a subject of such rapid growth the reviews have become outdated in certain aspects during the year pending unrevised re-issue. For example, in gas-liquid chromatography, the now established use of capillary or open tubular columns and ionisation detectors gains only cursory mention in Hardy and Pollard's paper.

The volume is well produced and is adequately indexed. The text is relatively free from errors as is to be expected for a second printing, but a few mistakes remain, *e.g.* "carbon monoxyde" on p. 131 and on p. 174 "ensuring" should presumably read "ensuing".

It is noted in the editor's preface that subsequent volumes of Chromatographic Reviews may not be entirely devoted to reviews previously published in the Journal of Chromatography. Such a change in policy is to be applauded; indeed it can be cogently argued that the wide, amorphous and rapidly expanding subject of chromatography could be better served by reserving Chromatographic Reviews entirely for original reviews not outdated as a result of prior publication elsewhere. The price of the present volume is high for reviews which have already been published, though the translations will be valuable to a number of chromatographic specialists.

J. K. FOREMAN

Optische Daten zur Bestimmung anorganischer Substanzen mit dem Polarisations-Mikroskop. ERNST KORDES. Verlag Chemie, Weinheim, 1960. Pp. xi + 192, with 8 separate Tables. DM 43.—.

THIS work will undoubtedly prove a valuable reference book for the practising chemical microscopist. It presents, systematically arranged, the optical properties of more than 1200 isotropic, uniaxial and biaxial inorganic materials, together with other properties (crystal form and habit, colour, melting point, hardness, solubility, density) that are of value in the identification of microscopic samples. Literature references are included for each substance.

In addition, the optical properties are arranged in condensed tabular form, and are also presented graphically as a series of separate folded diagrams contained in a pocket in the back cover.

The value of the book is enhanced by the provision of two admirable colour plates, showing the various types of interference figures, and by a really excellent summary, some twenty pages long, of the methods for determining optical properties using the polarising microscope. This last, although

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not full enough to satisfy a reader not already familiar with the principles of chemical microscopy, is nevertheless an excellent *aide memoire* or short "revision course" for anyone who has been out of practice with the methods for some time.

The author is to be congratulated on his work in collecting together and presenting in a single volume this mass of data which was previously scattered throughout a whole series of reference books, not all of them readily available. This book is for the chemist virtually an accessory to the polarising microscope.

CECIL L. WILSON

Crystals and the Polarising Microscope: A Handbook for Chemists and Others. Third Edition. N. H. HARTSHORNE and A. STUART. Edward Arnold (Publishers) Ltd., London, 1960. Pp. xv + 557. 80s.

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THIS book needs no introduction to chemists who have occasion to use the microscope, the earlier editions having established it securely as a classical contribution to the field of chemical microscopy. The fact that the present edition contains some hundred pages more than the second edition is some indication of the extent to which it has been revised, although the alterations are to a large extent in detail rather than identifiable as substantial additions. Special mention may be made, however, of the sections dealing with the mechanism of crystal growth, of the chapter dealing with the construction and use of the polarising microscope, of the inclusion of fusion methods, and of the additions to the applications, particularly with reference to fibres. Various rearrangements of material have also been made. These and similar alterations only serve to make the book even more valuable than it already was.

For anyone who wishes to keep completely up-to-date in this field, the new edition is essential, and can be thoroughly recommended.

CECIL L. WILSON

Talanta, 1961, Vol. 8, pp. 368 to 370. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Friday 9 *June* 1961: **Society for Analytical Chemistry,** Biological Methods Group: Summer visit to the Biological Laboratories, Research and Standards Departments, Boots Pure Drug Co. Ltd., Nottingham.

Wednesday 21 *June* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Discussion Meeting. *The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

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The eighty-seventh Annual General Meeting of the Society for Analytical Chemistry was held at Burlington House, London, W.I., on Friday, 3 March, 1961, with the President, Mr. R. C. CHIRNSIDE, in the Chair.

The following Officers and Members of Council were elected for the forthcoming year:

President:	A. J. AMOS
Past Presidents serving on the Council:	R. C. CHIRNSIDE, J. H. HAMMENCE, D. W. KENT-JONES, K. A. WILLIAMS.
Vice-Presidents:	A. L. BACHARACH, J. R. EDISBURY, F. C. J. POULTON.
Hon. Treasurer:	D. T. LEWIS
Hon. Secretary:	R. E. STUCKEY
Hon. Assistant Secretaries:	C. A. JOHNSON (Programmes), S. A. PRICE.
Ordinary Members of Council:	D. M. W. ANDERSON, B. BAGSHAWE, E. BISHOP, S. G. BURGESS, R. A. CHALMERS, D. C. GARRATT, S. H. JENKINS, E. Q. LAWS, W. M. LEWIS, C. A. PARKER, D. W. WILSON, J. T. YARDLEY.
Ex-Officio Members of Council:	J. MARKLAND (Chairman, North of England Section), A. F. WILLIAMS (Chairman, Scottish Section), G. V. JAMES (Chairman, Western Section), H. C. SMITH (Chairman, Midlands Section), C. WHALLEY (Chairman, Microchemistry Group), G. W. C. MILNER (Chairman, Physical Methods Group), J. S. SIMPSON (Chairman, Biological Methods Group).

The sixteenth Annual General Meeting of the Biological Methods Group of the Society for Analytical Chemistry was held on Thursday 8 December 1960 in *The Feathers*, Tudor Street, London, E.C.4. The Chairman of the Group, Dr. J. I. M. JONES, F.R.I.C. presided.

The following were elected Officers of the Group for the forthcoming year:

Chairman:	Mr. J. S. SIMPSON
Vice-Chairman:	Mr. W. A. BROOM
Hon. Secretary and Treasurer:	Mr. K. L. SMITH, Standards Department, Boots Pure Drug Co., Ltd., Nottingham, England.

The thirty-sixth Annual General Meeting of the North of England Section of the Society for Analytical Chemistry was held at the *Nag's Head Hotel*, Lloyd Street, Manchester, on Saturday, 28 January, 1961. The Chairman of the Section, Dr. J. S. Edisbury, presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman:	Mr. J. MARKLAND
Vice-Chairman:	Mr. C. J. HOUSE
Hon. Secretary and Treasurer:	Mr. B. HULME, Ch. Goldrei, Foucard and Son Ltd., Brookfield Drive, Liverpool, 9.

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The twenty-sixth Annual General Meeting of the Scottish Section of the Society for Analytical Chemistry was held at the *Grosvenor Restaurant*, Gordon Street, Glasgow, on Thursday, 26 January, 1961. The Chairman of the Section, Mr. A. N. HARROW, presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman:	Mr. A. F. WILLIAMS
Vice-Chairman:	Dr. R. A. CHALMERS
Hon. Secretary and Treasurer:	Mr. J. BROOKS, Research and Development Department, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire.

The sixth Annual General Meeting of the Midlands Section of the Society for Analytical Chemistry was held at Regent House, St. Philips Place, Birmingham, on Tuesday, 14 March, 1961. The Chairman of the Section, Dr. S. H. JENKINS, presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman:	Dr. H. C. SMITH
Vice-Chairman:	Mr. W. H. STEPHENSON
Hon. Secretary:	Mr. G. W. CHERRY, 48, George Frederick Road, Sutton Coldfield, Warwickshire.
Hon. Treasurer:	Mr. F. C. POULTON.

The following new British Standards are announced in B.S.I. News:

B.S. 1121: *Methods for the analysis of iron and steel: Part* 42: 1961: *Cobalt in iron and steel.* This specifies a method for the photometric determination of trace amounts of cobalt in commercially-pure iron and all types of steel containing cobalt within the range 0·002% to 0·04% of cobalt. (Price 3s.)

B.S. 1748: *Methods for the analysis of copper alloys: Parts* 1–5: 1961: *Methods for the determination of copper, lead, iron, aluminium and nickel in copper alloys.* This specifies reagents required, recommended methods of sampling and test procedure from one sample weighing for the determination of copper, lead, iron, aluminium and nickel, in copper alloys containing 1 to 14% of tin, 1 to 2% of nickel, and small amounts of aluminium, *e.g.* phosphor bronzes, leaded phosphor bronzes, gun metals and leaded gun metals. (Price 6s.)

B.S. 3334: 1961: *Method for the quantitative chemical analysis of mixtures of cellulose triacetate and secondary cellulose acetate fibres.* This provides a method for determining the proportions of the two components in mixtures of these fibres. It is based on dry-weights but a formula is also given for reporting the results including additions to compensate for moisture.

The method is suitable for application to fibres in any textile form, *i.e.* tow, sliver, roving, yarn or fabric. (Price 4s.)

B.S. 3336: 1961: *Method for the quantitative chemical analysis of ternary mixtures of protein fibres, polyamides and certain other fibres.* This provides a method for determining the proportions of the three components in mixtures of these types of fibres.

Formulae are given for expressing the results either on the basis of dry-weights or of corrected invoice weights.

The method is suitable for application to fibres in any textile form, *i.e.* tow, sliver, roving, yarn or fabric. (Price 3s.)

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys: Part 1:* 1961: *Sampling of ingot tin.* This specifies sampling of ingots, preparation of surfaces, method of taking samples by means of sawing, and precautionary measures against contamination of the sawings. (Price 3s.)

Part 2: 1961: *Tin in ingot tin* (*aluminium reduction method*). This specifies reagents required, recommended methods of sampling and test procedure for the determination of tin in ingot tin having a tin content from 99·0 to 99·8%. (Price 4s.)

Part 7: 1961: *Silver in solders* (*volumetric: ammonium thiocyanate method*). This specifies reagents required, recommended methods of sampling and test procedure for the determination of silver in solders having a silver content up to 3%. (Price 3s.)

Part 11: 1961: *Tin in solders* (*nickel coil reduction method*). This specifies reagents required, recommended methods of sampling and test procedure for the determination of tin in solders having a tin content exceeding 1%. (Price 3s.)

Part 12: 1961: *Sampling of solders.* This specifies selection of ingots, bars, sticks or wire, preparation of sample, preparation of surfaces, methods of taking final samples by means of sawing, as well as precautionary measures against contamination of the sawings. (Price 3s.)

B.S. 3344: 1961: *Method for the quantitative chemical analysis of binary mixtures of cellulose triacetate and certain other fibres.* This provides a method for determining the proportions of the two components in mixtures of these fibres. It is based on dry-weights but a formula is also given for reporting the results including additions to compensate for moisture. The method is suitable for application to fibres in any textile form, *i.e.*, tow, silver, roving, yarn or fabric. (Price 4s. 6d.)

The following revised British Standard is announced:

B.S. 1583:1961: *One-mark pipettes.* Thirteen sizes of pipette from 0·5 ml to 200 ml are specified, all being of the bulb pattern except that the 0·5-ml size is a straight pipette and that both bulb and straight patterns are permitted for Classes A and B pipettes of the 1-ml size and Class B pipettes only of the 2-ml size. Full dimensions are given but only the essential ones are listed as mandatory, the remainder being given for the guidance of manufacturers. Standard methods are included for the determination of capacity and delivery time and tolerances are listed for both. (Price 4s.)

The following amendment slip is announced:

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 12: 1959: *Caking and swelling properties of coal. Amendment No.* 1: *PD* 4005. (Gratis)

Part 15: 1960: *Fusibility of coal ash and coke ash. Amendment No.* 1: *PD* 4004. (Gratis)

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PAPERS RECEIVED

Analytical applications of the reagent Arsenazo-III: Determination of thorium, zirconium and rare-earth elements: S. B. SAVVIN. (22 *February* 1961).

Studies on uronic acid materials—III: The use of ^{14}C compounds to determine acid decarboxylation reaction times: D. M. W. ANDERSON and S. GARBUTT. (4 *March* 1961).

The determination of thiol compounds. J. M. BAKES and P. G. JEFFERY. (6 *March* 1961).

Estimation of xanthate and dixanthogen: S. RAMACHANDRA RAO. (6 *March* 1961).

Photometric titrations—II: Design and construction of a photometric titrator: H. FLASCHKA and P. SAWYER. (6 *March* 1961).

Determination of radiophosphorus by solvent extraction. HARLEY H. ROSS and RICHARD B. HAHN. (2 *March* 1961).

Isotopic dilution analysis by ion-exchange: Determination of traces of iron: JIŘÍ STARÝ and JAROMÍR RŮŽIČKA. (10 *March* 1961).

Spectrographic analysis of gallium and indium with extraction: JERZY MINCZEWSKI, HANNA MALESZEWSKA and TERESA STECIAK. (11 *March* 1961).

Spectrophotometric and potentiometric studies on the composition of iron complexes of potassium octacyanomolybdates: WAHID U. MALIK and S. IFTIKHAR ALI: (14 *March* 1961).

The determination of rhenium in rocks by neutron-activation analysis: D. F. C. MORRIS and F. W. FIFIELD. (14 *March* 1961).

Der Aufbau einiger Metall-Carbamatverbindungen: H. MALISSA and H. KOLBE. (15 *March* 1961).

Coulometric titration by electrogenerated stannous ion: TAKEO TAKAHASHI and HIROSHI SAKURAI. (15 *March* 1961).

Coulometric titration of hydroxylamine and hydrogen peroxide by electrogenerated ceric ion: TAKEO TAKAHASHI and HIROSHI SAKURIA. (20 *March* 1961).

Spectrophotometric determination of bismuth with Xylenol Orange after Dithizone-chloroform extraction: HIROSHI ONISHI and NASUMI ISHIWATARI. (20 *March* 1961).

Spectrophotometric determination of vanadium with 3,3′-diaminobenzidine: K. L. CHENG. (24 *March* 1961).

Sur un principe de colorimétrie en milieux non-aqueux—III: L'emploi du chlorure de p-nitrophénylazo benzoyle pour le dosage des amines primaires et sécondaires: JAROSLAV BARTOS. (24 *March* 1961)

5-Amino-2-benzimidazolethiol as an analytical reagent—I: Spectrophotometric determination of palladium. J. G. SEN GUPTA. (27 *March* 1961).

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THE TALANTA MEDAL, 1961

Professor R. BELCHER (U.K.) Chairman of the Advisory Board of Talanta and President of the Analytical Chemistry Section of I.U.P.A.C., delivers the citation preceding the presentation of the Talanta Medal to Professor FRITZ FEIGL (Brazil). The presentation took place in the Ceremonial Hall of the Hungarian Academy of Sciences during the opening of the Analytical Chemistry Congress of the Hungarian Chemical Society. The Congress was held in Budapest on 24–29 April 1961. Others, left to right, at the table are Mr. S. CZOTTNER (Hungarian Minister for Heavy Industry), Professor G. SCHAY (President of the Hungarian Chemical Society) and Professor I. RUSZNYAK (President of the Hungarian Academy of Sciences).

The conditions of award of the Talanta Medal were set forth in Talanta, 1959, **3**, 217. Announcement of Professor FEIGL (Brazil) as the first recipient was made in Talanta, 1961, **8**, 170.

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Professor BELCHER (U.K.) presents the Talanta Medal to Professor FEIGL (Brazil) while the President of the Hungarian Academy of Sciences looks on.

Professor E. SCHULEK (Hungary) extends to Professor FEIGL (Brazil) congratulations from the Analytical Chemistry Congress.

Mrs. SZABÓ (Hungary), Professor L. GORDON (U.S.A.), Regional Editor of Talanta and Secretary of the Analytical Chemistry Section of I.U.P.A.C., and Professor BELCHER (U.K.) examine the Talanta Medal with Professor FEIGL (Brazil).

Professor L. ERDEY (Hungary) demonstrates the use of the derivative thermogravimetric balance to Professor FEIGL (Brazil).

Professor K. JACIMIRSKIJ (U.S.S.R.) discusses common interests in analytical chemistry with Professor GORDON (U.S.A.). Professor JACIMIRSKIJ will be visiting U.S.A. for the Sixth International Conference on Co-ordination Chemistry at Detroit, Michigan, from 27 August to 2 September, 1961. Both Professors delivered Plenary Lectures at the Congress.

All photographs of the Analytical Chemistry Congress of the Hungarian Chemical Society were taken by JENÖ ICZKOVITS and JOZSEF FARKAS.

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THE DETERMINATION OF TRACES OF IRIDIUM IN SAMPLES OF RHODIUM BY NEUTRON-ACTIVATION AND GAMMA-RAY SPECTROMETRY

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(*Received* 17 *October* 1960. *Accepted* 31 *October* 1960)

Summary—Neutron-activation analysis has been applied to the determination of traces of iridium impurity in specimens of rhodium. The Harwell Pile BEPO has been used as neutron source. The method involved irradiation of samples and standards and their subsequent γ-spectrometric assay; no radiochemical separations were required.

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IN a recent paper Morris and Killick[1] have given details of the determination of traces of iridium in palladium and platinum by neutron-activation analysis. The method described involved radiochemical separation of the induced iridium activities using carriers. In the present work, the analysis of traces of iridium in rhodium by neutron-activation, without any chemical processing, is described.

The nuclear characteristics of the isotopes involved when iridium is subjected to bombardment with neutrons of thermal energies are given in Table I.

TABLE I.—NUCLEAR DATA FOR IRIDIUM

Target nuclide	Abundance of nuclide in natural element, %	Isotopic activation cross-section, *barns*	Product of thermal neutron irradiation	Radiation and energy of product nuclide, *MeV*	Half-life of product radionuclide
^{191}Ir	38·5	260	^{192m}Ir	IT e$^-$(γ) 0·056 (^{Q}IT)(99·9%); β^-0·056 (*ca.*0·1%)	1·42 min
		700	^{192}Ir	β^-0·097 (1%), 0·26 (8%), 0·54 (35%), 0·67 (50%); EC (6%); γ0·136, 0·296, 0·308, 0·316, 0·468, 0·604, others.	74 d
^{193}Ir	61·5	130	^{194}Ir	β^- 2·24 (66%), 1·91 (15%), 0·98 (10%), 0·43 (*ca.* 8%); γ 0·329 (others 0·29 to 2·05)	19 hr

EXPERIMENTAL

Specimens of rhodium for analysis were in powder form and *ca.* 0·1-g samples were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Iridium and rhodium both have large absorption cross sections[2] for thermal neutrons, 440 and 156 barns respectively. To avoid neutron self-shielding differences between samples and standards, therefore, standards were prepared by the admixture of small known quantities of iridium with analytical samples. This was done by adding weighed portions of dilute solutions of iridium [as $(NH_4)_2IrCl_6$ in 3*M* HCl] to *ca.* 0·1-g samples of rhodium in silica tubes of 4-mm internal diameter. The liquid was allowed to soak into

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the metal powder, and then was carefully evaporated to dryness, after which the tubes were sealed. In the preparation of the standards, weights of iridium added were about 50% of the weights of the element expected to be present in the samples.

Samples, together with standards containing added iridium, were packed with silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron irradiation. Irradiations were for periods up to 1 week in the Pile BEPO with a thermal neutron flux of 10^{12} neutrons per cm^2 per sec.

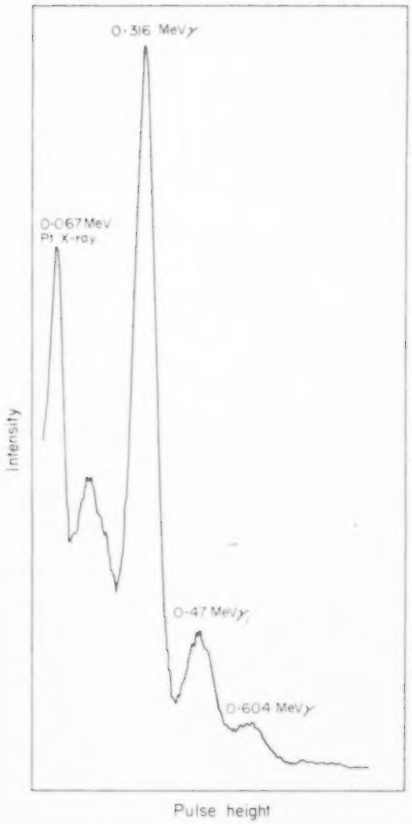

Fig. 1—γ-Ray spectrum of pure iridium-192.

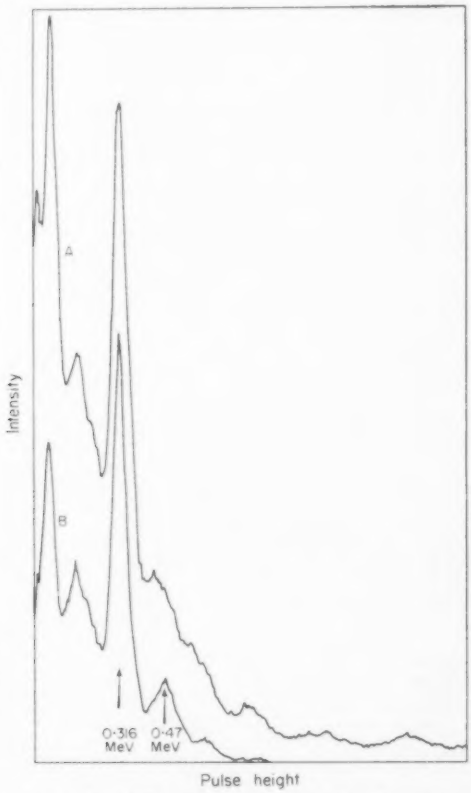

Fig. 2—γ-Ray spectra of a sample of neutron irradiated rhodium:
A—on first day from end of irradiation.
B—on eighth day from end of irradiation.

After irradiation, samples and standards were removed from the silica tubes and distributed uniformly over aluminium counting trays (A.E.R.E. cat. no. 4-3/1068). The silica tubes were rinsed out with hot water, and the resulting slurries on the counting trays were evaporated to dryness under a radiant-heater lamp. (A preliminary experiment with iridium-192 tracer showed that the added iridium in irradiated standards was completely transferred from the silica tubes to the counting trays by this technique). The material on the trays was covered with Sellotape.

After 8 days from the end of neutron-irradiation, the samples and standards were measured at constant geometry with a γ-ray spectrometer. The instrument used consisted of a 1-inch $\times$ 1½-inch thallium-activated sodium iodide crystal mounted on a 6097B E.M.I. photomultiplier tube. After amplification, the output pulses from the photomultiplier were passed into a single-channel pulse analyser and thence to a ratemeter. The output was fed into a recording potentiometer ganged to the

analyser bias sweep. In this manner it was possible to obtain a γ-ray spectrum as a plot of counting rate *vs.* pulse height.

The intensities of the photo-peaks corresponding to γ-rays of 0·316 and 0·47 MeV were measured in arbitrary units for samples and standards in turn. From the measured peak-heights, and the known weights of samples and standards and the known amounts of added iridium in the standards, the iridium contents of the samples could be calculated.

DISCUSSION AND RESULTS

The γ-ray spectrum of pure iridium-192 is shown in Fig. 1. Spectra of a sample of neutron-irradiated rhodium are shown in Fig. 2.

TABLE II.—RADIONUCLIDES PRODUCED BY (n,γ) OR U(n,f) REACTIONS GIVING γ-RAYS WHICH COULD NOT BE DIFFERENTIATED FROM THE 0·316 MeV IRIDIUM-192 γ-RAY

Nuclide	Half-life	Mode of formation	γ-ray energy, *MeV*
^{160}Tb	73·5 d	^{159}Tb(n,γ)	0·299
^{140}Ba	12·8 d	U(n,f)	0·304
^{233}Pa	27·4 d	^{232}Th(n,γ)^{233}Th(β^-)	0·301, 0·313
^{51}Cr	27·8 d	^{50}Cr(n,γ)	0·320, 0·325
^{105}Rh	36·5 hr	^{104}Ru(n,γ)^{105}Ru(β^-)	0·320
^{193}Os	30·6 hr	^{192}Os(n,γ)	0·321
^{140}La	40·0 hr	^{140}Ba(β^-) ^{139}La(n,γ)	0·3286

Measurements of the decay of the peaks at 0·316 and 0·47 MeV for samples of neutron-irradiated rhodium showed that after 8 days from the end of irradiation only γ-rays from ^{192}Ir were being counted.

Other activities which, after 8 days "cooling", could possibly have interfered with the measurement of the 0·316 MeV and 0·468 MeV γ-rays of ^{192}Ir are shown in Tables II and III.

Some analytical results are shown in Table IV.

TABLE III.—RADIONUCLIDES PRODUCED BY (n,γ) OR U(n,f) REACTIONS GIVING γ-RAYS WHICH COULD NOT BE DIFFERENTIATED FROM THE 0·468 MeV IRIDIUM-192 γ-RAY

Nuclide	Half-life	Mode of formation	γ-ray energy, *MeV*
^{110m}Ag	270 d	^{109}Ag(n,γ)	0·446
^{131}Te	24·8 min	^{130}Te(n,γ) ^{131m}Te(IT)	0·45
^{193}Os	30·6 hr	^{192}Os(n,γ)	0·46
^{187}W	24·0 hr	^{186}W(n,γ)	0·4795
^{131}Ba	11·5 d	^{130}Ba(n,γ)	0·498
^{140}La	40·0 hr	^{140}Ba(β^-), ^{139}La(n,γ)	0·487
^{103}Ru	39·8 d	U(n,f)	0·498

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Table IV.—Iridium contents of some specimens of rhodium determined by neutron-activation and γ-spectrometric analysis

Specimen	Iridium content found from 0·316-MeV photopeak, *ppm*	Iridium content found from 0·468-MeV photopeak, *ppm*
Rh 1	172	171
	173	174
	168	169
	168	166
Rh 2	137	135
	146	145
	141	136
	136	134
Rh 10 (very high purity)	3·36	3·6
	3·93	4·2
	3·13	3·6

Acknowledgements—Grateful acknowledgement is made to The Mond Nickel Company Ltd for the loan of specimens of rhodium, for financial support, and for a Research Fellowship to one of us (R. A. K.).

We are indebted to Dr. G. L. Reed for making some valuable modifications to the γ-ray spectrometer.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Iridiumspuren in Rhodiumproben herangezogen. Der Harwellofen BEPO wurde als Strahlenquelle verwendet. Die Methode beschränkt sich auf Bestrahlung von Probe und Standard und anschliessender Zählung der Gammastrahlen; keine radiochemische Trennung ist nötig.

Résumé—L'analyse par activation de neutrons a été appliquée au dosage de traces d'impureté d'iridium dans des échantillons de rhodium. La pile BEPO de Harwell a été utilisée comme source de neutrons. La méthode fait intervenir l'irradiation des échantillons et des témoins puis leur dosage par spectrométrie γ; aucune séparation radiochimique n'a été nécessaire.

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THERMOGRAVIMETRIC DECOMPOSITION OF THORIUM 8-HYDROXYQUINOLATE*

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(*Received* 29 *November* 1960. *Accepted* 30 *January* 1961)

Summary—The thermogravimetric behaviour of crystalline thorium 8-hydroxyquinolate has been correlated with empirical and molecular formulae. The first of two sharp breaks is shown to be due to both water and oxine, and the second to oxine alone.

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INTRODUCTION

THERMOGRAVIMETRIC curves for the decomposition of the 8-hydroxyquinolates of various metals have been reported in a number of investigations. Frere,[1] Dupuis and Duval,[2] Borrell and Pâris,[3] and Wendlandt,[4] in particular, have included the thorium 8-hydroxyquinolate in their studies.

There has been considerable interest in obtaining spherical particles of thorium oxide and mixed thorium-uranium oxides for use as a slurry reactor fuel. In the precipitation of thorium from homogeneous solution with 8-acetoxyquinoline, as reported by Salesin and Gordon[5] and Takiyama, Salesin and Gordon,[6] it was noted that the precipitate obtained appeared in the form of uniformly-sized spherical particles several hundredths of a mm in diameter. The particle geometry was not preserved, however, on heating above the decomposition temperature of the thorium 8-hydroxyquinolate.

Also, because some difficulty had been observed previously in obtaining reproducible breaks in the thermogravimetric curves,[1–4] it was of interest to repeat the pyrolysis on the relatively large crystalline precipitate obtained with the precipitation from homogeneous solution.

EXPERIMENTAL

The 8-acetoxyquinoline was obtained from the Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Michigan. The melting point was 56°. An infrared spectrum was supplied to demonstrate the absence of 8-hydroxyquinoline with a melting point of 73°. A comparison of the two infrared spectra has been given by Salesin and Gordon.[5]

The precipitation from homogeneous solution of thorium 8-hydroxyquinolate was made in the following manner:

Three g of 8-acetoxyquinoline were dissolved in a mixture of 30 ml of glacial acetic acid and 30 ml of water in a 1-litre breaker; 500 ml of water were added. Then 25 ml of thorium nitrate stock solution, containing 600 mg of thorium, were added, and the pH was adjusted to 5·3 with ammonium hydroxide. The solution was heated to 50° and kept at this temperature for 2 hr. The precipitate appeared in about 10 min and was complete in about 2 hr. The cooled mixture was centrifuged, and washed twice with cold distilled water.

The washed precipitate was dried for several days at room temperature in a vacuum desiccator. Drying was also done on the original precipitate in the balance chamber over-night, with dry argon sweep gas at room temperature; and a third procedure was drying at 50° for up to 24 hr with a sweep gas.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

The balance used for the thermogravimetric pyrolysis studies was a Sartorius Selecta balance equipped with recording attachment and amplifier. The output of the amplifier was displayed on a Bristol Dynamaster recording potentiometer giving a continuous record of weight change *vs.* time. The sample-pan was suspended by a nickel chain into the reaction furnace, situated directly below the balance. Hot convection currents from the furnace were kept out of the balance by a baffle and gas blanket arrangement. A gas distribution manifold allows a choice of reaction gas. All gases passed through a preheat furnace before entering the main reaction furnace. The sample temperature was measured by a calibrated thermocouple positioned directly beneath the sample-pan.

The temperature rise of the furnace was controlled by a West pyrometer controller. A standard heating rate of 3° per min, and a 300-mg sample were used in all experiments. The 300-mg sample was spread evenly over an area of about 3 cm².

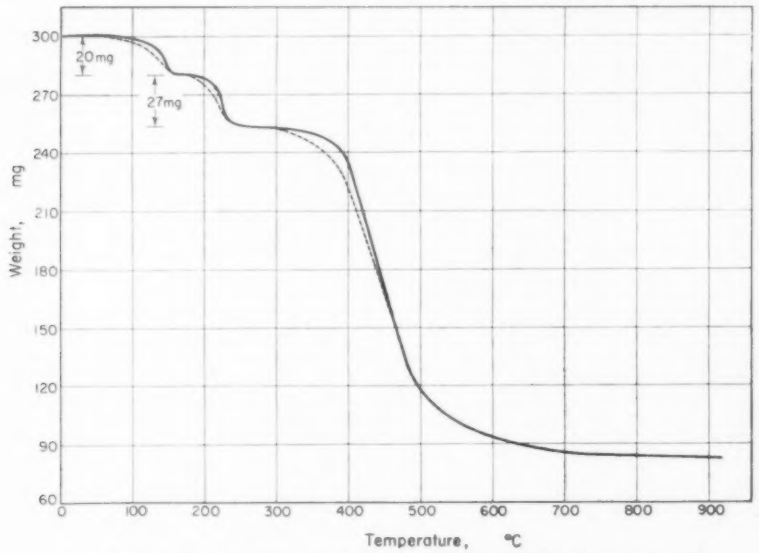

FIG. 1.—Thermal decomposition curve of thorium 8-hydroxyquinolate
——— precipitate from homogeneous solution
– – – – conventional precipitate.

In addition to the thermogravimetric behaviour, the thorium and oxine content of the solid were determined after heating at the plateaus of thermal stability. Analyses were made, both on samples that were removed from the thermobalance by stopping the run at a plateau, and on samples that had been heated in a separate apparatus to the temperature of the plateau on the thermogram.

The thorium content was determined by an air ignition at 950° to yield thorium dioxide. The oxine content was obtained spectrophotometrically. A known quantity of thorium 8-hydroxyquinolate was dissolved in 0·1*N* HCl and diluted to a known volume. The acid decomposes the thorium complex, but yields a solution of the 8-hydroxyquinoline which is stable for days. At lower acid concentration the presence of the thorium in solution may enhance the absorbance due to oxine alone. At the low thorium concentrations involved here, however, and in 0·1*N* HCl, no effect was observed. Crystals of the pure 8-hydroxyquinoline were dissolved in 0·1*N* HCl and diluted to a known volume for use as standards. A Model 11 Cary recording spectrophotometer was employed to record the oxine spectrum in the region of 400 to 290 mμ.

A vertical furnace equipped with a large Pyrex tube was employed, so that material which sublimed or vaporised, in the heating of weighed samples of thorium 8-hydroxyquinolate at a given temperature, could be condensed on a cold section and removed for analysis. The breaks shown in Fig. 1 were easily associated with the appearance of a ring of condensed water vapour and/or 8-hydroxyquinoline crystals on the wall of the cold section of the Pyrex tube. The temperature rise was

arrested at about the point of the maximum slope (Fig. 1), and the condensate was collected for a few additional min.

DISCUSSION

The analysis of the condensate on the Pyrex tube walls, summarised in Table I, demonstrated very clearly that the first break yielded two products, water and crystalline 8-hydroxyquinoline. This result was obtained on material that had been dried at 50° for up to 24 hr, and also on material dried at room temperature (25°) in a vacuum for 24 hr. The droplets of water vapour condensate were easily distinguished from the sharp needle-like crystals of oxine on the Pyrex tube wall. In slow heating, it was observed that some oxine crystals formed on the cold wall before the appearance of water droplets, but it was not possible to obtain a clearly observable thermal plateau for each product lost in the first thermal break.

Only the needle-like crystals of oxine were observed to condense on the tube wall at the second break in the curve. Analysis of the condensate substantiated the view that the total weight loss at this temperature was due solely to oxine. At both temperatures, the visible and ultraviolet spectra of the condensate indicated no evidence of degradation of the oxine.

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TABLE I.—SUMMARY OF THE ANALYSIS OF THORIUM 8-HYDROXYQUINOLATE SOLIDS AND THEIR FURNACE CONDENSATES AFTER HEATING AT THE THERMAL PLATEAUS

Empirical formulae	Numerical results given for analysis of 300-mg samples	
	Analytical results[d] with standard deviation	Weight losses calculated from postulated formulae
$Th(Ox)_{4\cdot8}\cdot 2H_2O$ M.W. = 960 (yellow)	Analysis of the oxine and thorium content gave 4·80 ± 0·03[a]	Precipitates dried below 50° in air or vacuum for 24 hr.
$Th(Ox)_{4\cdot6}$ M.W. = 895 (yellow-green)	H_2O[c] 11·4 ± 0·3 mg *Oxine*[b] 8·9 ± 0·15 mg *Thermograv. loss* 20·0 ± 0·2 mg $\frac{Oxine}{Th}$ = 4·60 ± 0·05	H_2O 11·2 mg *Oxine* 9·00 mg *Thermograv. loss* = 20·2 mg *Max. temperature employed* 165°
$Th(Ox)_{4\cdot0}$ M.W. = 809 (green)	*Thermograv. loss* 27·0 ± 0·3 mg *Oxine*[b] 27·3 ± 0·4 mg $\frac{Oxine}{Th}$ = 4·00 ± 0·05	H_2O 0·0 *Oxine* 27·0 mg *Thermograv. loss* = 27·0 mg *Max. temperature employed* 230°

[a] Takiyama, Salesin and Gordon[6] have also obtained a value of 4·8 on crystalline material formed by precipitation from homogeneous solution.

[b] Oxine on furnace walls determined spectrophotometrically.

[c] Mg of water obtained by the difference of losses observed in the thermogravimetric analysis at the first break shown in Fig. 1 and the oxine loss obtained by analysis of the Pyrex tube wall deposits.

[d] Analytical results are summarised from 5 experiments using 3 different samples each precipitated from homogeneous solution. One sample was furnished by Louis Gordon, Case Institute of Technology, Cleveland, Ohio.

It was also observed that the original material [$Th(OX)_{4\cdot8}\cdot 2H_2O$] was quite soluble in dry methyl alcohol, yielding a yellow solution. However, the same rearrangement, or a very similar rearrangement to that which had occurred on heating, took place rapidly in solution. Shortly a new precipitate appeared which, when

analysed, indicated a mole ratio of oxine to thorium of 4:1. Large amounts (1·0 g) of the hydrated thorium oxine, when stirred with approximately 100 ml of dry methyl alcohol for about one hour, were converted completely to $Th(Ox)_4$ by a continuous dissolution and re-precipitation. This may offer a precise method of adjusting the thorium oxine stoichiometry, since the released excess oxine and water appear to be more easily volatilised with the alcohol at 100° or less.

No effort has been made to make detailed comparisons of various thermogravimetric values. Borrell and Pâris[3] and Wendlandt[4] and this work are all in general agreement that the normal thorium oxinate, $Th(Ox)_4$, is obtained by heating at or slightly above 275°, 250° and 225° respectively. Takiyama, Salesin and Gordon,[6] however, with conventional drying for 10 hours at 180°, also have obtained the normal thorium oxinate. The rate of decomposition of a solid, and in turn the effect as reflected in thermogravimetric curves, has been neglected in many studies. This has led to difficulties in relating thermogravimetric behaviour to conventional gravimetric analysis. It is appropriate to point out that precise designation of reaction temperatures by thermogravimetric analysis is problematical, and is dependent on the experimental conditions used. This point is discussed by Markowitz and Boryta.[8]

The lack of agreement in attaining the thorium oxide level has been pointed out by Wendlandt.[4] In this work we have not been able to obtain a stable thorium oxide level in the thermogravimetric balance in the 600–700° range, as reported by both Wendlandt,[4] and Borrell and Pâris.[3] Dupuis and Duval[2] found that a stable oxide level was not obtained at 945°. A similar problem in the minimum ignition temperature of aluminium oxide has been studied by Milner and Gordon.[7]

Zusammenfassung—Die thermogravimetrische Zersetzung von kristallinem Thoriumoxinat wurde mit empirischen und Molekularformeln korreliert. Der erste von zwei scharfen Knicken wird durch Wasser und Oxin, der zweite durch Oxin allein verursacht.

Résumé—Les auteurs ont relié la décomposition thermogravimétrique du composé cristallin thorium-8 hydroxyquinoléine aux formules empirique et moléculaire. On montre que la première des deux cassures nettes est due à l'eau et à l'oxine, et la sedonde à l'oxine seule.

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PHOTOMETRISCHE TITRATIONEN—I

ALLGEMEINE BETRACHTUNGEN UND DIE THEORIE CHELOMETRISCHER TITRATIONEN OHNE ANWENDUNG EINES INDICATORS

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Zusammenfassung—Es werden Besonderheiten von chelometrischen Titrationen mit photometrischem Endpunkt ohne Indicator aufgezeigt. Formeln zur Berechnung der Titrationskurven werden abgeleitet. Es wird gezeigt, dass im Falle der Titration eines einzelnen Metalles eine wesentlich geringere Stabilität des Titrationskomplexes toleriert werden kann, als bei anderen Endpunktsmethoden, die nicht auf Extrapolation beruhen. Für die Titration zweier Metalle hintereinander in ein und derselben Lösung ist ein Unterschied (Quotient) in den Stabilitätskonstanten von etwa 100–200 ausreichend. Möglichkeiten der photometrischen Indication ohne Indicator in Kombination mit anderen Endpunktsmethoden werden diskutiert und vom Standpunkt des Selektivitätsproblemes aus betrachtet.

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IN einer seinerzeit erschienenen Arbeit hat der Autor die Endpunktstheorie chelometrischer Titrationen behandelt.[1] Formeln wurden abgeleitet, anhand derer man die Titrationsbedingungen, Genauigkeit usw. errechnen kann. Die Behandlung des Stoffes wurde aufgrund der Beziehungen zwischen Volum an Masslösung und pM(= $-\log$ M) durchgeführt. Es war eindringlich darauf verwiesen worden, dass die Verhältnisse eine einschneidende Änderung erfahren, wenn der Endpunkt ohne einen visuellen Indicator ermittelt wird und dass im besooderen die Anwendung graphischer Methoden dazu führt, dass weniger strikte Bedingungen für die Durchführung der Titration toleriert werden können.

Grundsätzlich muss zwischen zwei verschiedenen graphischen Methoden unterschieden werden. Die eine Gruppe von Methoden umfasst solche, die "im Endpunkte" arbeiten, wie z.B. potentiometrische Titrationen. Hier wird der Wendepunkt in der Titrationskurve ermittelt und zwar aus dem Kurventeil nahe vor und nach dem Endpunkt. Unter diesen Bedingungen wird jener Teil der Kurve verwendet, wo das Gleichgewicht des zu messenden Systems in einem ungünstigen Mittelstadium schwebt und den höchsten Grad der Dissoziation des Titrationskomplexes aufweist. Die zweite Gruppe von Methoden verwendet zur Ermittlung des Endpunktes eine Extrapolation. Der eine Kurvenast, der zur Extrapolation herangezogen wird, liegt im Bereich, wo Metallionen im Überschuss vorhanden sind und somit das Gleichgewicht nach der Seite geringerer Dissoziation des Titrationskomplexes verschoben ist. Der zweite Ast liegt im Bereich, wo Titrationsmittel im Überschuss vorhanden ist und auch hier ist das Gleichgewicht in günstigem Sinne nach der Richtung geringerer Dissoziation des Titrationskomplexes verschoben. Methoden, die nach diesem Gesichtspunkte arbeiten, sind z.B. Leitfähigkeits-, amperometrische und photometrische Titrationen.

Soweit es photometrische Titrationen schwacher Säuren und Basen betrifft, sind zahlreiche Beispiele in der Literatur vorhanden, die eindeutig den enormen Vorteil

dieser Methode demonstrieren. Auch die theoretischen Grundlagen solcher Titrationen sind bearbeitet worden. Ein ausgezeichneter Artikel von Goddu und Hume[2] behandelt diese Art von Titrationen eingehend. Andere Autoren haben wesentlich zu diesem Gebiete beigetragen.[3,4] Eine letztlich erschienene Zusammenfassung von Headridge[5] bringt ein bis auf die jüngste Zeit vollständiges Literaturverzeichnis.

Goddu und Hume[2] haben darauf verwiesen, dass eine ähnliche Behandlung, wie sie für Säure-Basentitrationen gegeben wurde, auch für komplexometrische Titrationen möglich ist. Es wurde jedoch bislang die Theorie komplexometrischer Titrationen ohne Indicator nicht im Detail durchgearbeitet. Wohl aber existiert eine Behandlung für Titrationen mit einem Indicator.[6]

Bereits nur anfänglich angestellte Berechnungen zeigten sehr rasch, dass die Möglichkeiten komplexometrischer Titrationen ohne Indicator und mit photometrischem Endpunke sehr unterschätzt worden sind. Photometrische Endpunktsanzeige *mit* einem Indicator wurden häufig verwendet und zwar immer dann, wenn es sich um einen für das Auge schleppenden Umschlag handelt oder aber, wenn kleine Stoffmengen zu titrieren waren, so dass Indicator und zu titrierendes Metall bereits in vergleichbaren Mengen vorlagen. Auch zur Erzielung höherer Genauigkeit, bei an sich recht gut arbeitenden Indicatoren, wurden solche Titrationen herangezogen.[7–13]

Im Hinblick auf zwei wichtige Punkte jedoch sind Untersuchungen vernachlässigt worden. Einmal sollte es möglich sein, aus der Extrapolationsmethode Kapital zu schlagen und Komplexbildner zur Titration heranziehen, die so schwache Komplexe bilden, dass mit visueller Indication kein befriedigendes Resultat zu erhalten ist. Zweitens aber sollte es möglich sein, dem Selektivitätsprobleme näher zu treten, wie aufgrund der in der oben erwähnten, früheren Arbeit vorauszusehen war. Im Falle einer Titration ohne Indicator ist der zur Titration von zwei Metallen (in derselben Lösung) nötige Unterschied in den beiden Stabilitätskonstanten wesentlich geringer. Beide Möglichkeiten liessen sich aus einigen Beispielen in den Arbeiten erkennen, die über photometrische Titrationen ohne Indicator veröffentlicht wurden.[14–17]

In welchem diese Möglichkeiten praktische Anwendung finden können und was zu ihrer Abschätzung an theoretischem Rüstzeug benötigt wird, soll hier nunmehr behandelt werden.

(A) *Chelometrische Titration eines Metalles ohne Indicator*

Es sei angenommen, dass ein Metall M mit einem Komplexbildner Y titriert wird, wobei ein 1:1 Komplex nach der Gleichung

$$M + Y \rightleftharpoons MY \qquad (I)$$

gebildet wird. Ladungszeichen, weil für den Prozess der Komplexbildung unwesentlich, sind weggelassen.

Im allgemeinsten Falle muss angenommen werden, dass alle drei vorhandenen Teilchenarten bei der gewählten Wellenlänge absorbieren. Wird die Gültigkeit von Beer's Gesetz vorausgesetzt, dann ist die gemessene Gesamtabsorption gleich der Summe der Teilabsorptionen, was mathematisch wie folgt ausgedrückt werden kann:

$$A = \sum_i \epsilon_i [i] \, l \qquad (1)$$

Hier bedeuten A die Totalabsorption, ϵ den molaren Extinktionskoeffizienten, [i] die Konzentration der Spezie *i* in Mol per Liter und l die Länge des Lichtweges. Da während einer Titration die Länge des Lichtweges konstant ist, kann Gleichung (1) für

alle weiteren Zwecke vereinfacht werden, indem man $\varepsilon_i \times 1 = k_i$ zusammenfasst, womit sich ergibt:

$$A = \sum_i k_i[i] \tag{2}$$

In jeder Phase der Titration müssen die folgenden beiden Gleichungen erfüllt sein:

$$C_M = [M] + [MY] \tag{3}$$

$$C_Y = [Y] + [MY] \tag{4}$$

Als weitere Gleichung kommt noch die Definition der Stabilitätskonstante des Komplexes hinzu, nämlich

$$K = \frac{[MY]}{[M][Y]} \tag{5}$$

Es sei ausdrücklich darauf verwiesen, dass es sich hier um die *scheinbare* Stabilitätskonstante handelt, die aus der absoluten Konstante durch einbezug des α- und β-Faktors errechnet werden kann, um dem Einfluss des pH der Lösung sowie der Anwesenheit allenfalls vorhandener, weiterer Komplexbildner Rechnung zu tragen. Über Berechnungen dieser Art siehe.[18,19]

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Die bisher gegebenen Gleichungen genügen um eine photometrische Titrationskurve zu berechnen. Im einzelnen verläuft die Ableitung wie folgt. Gemäss (2) gilt für den in (I) dargelegten Fall

$$A = [M]k_M + [MY]k_{MY} + [Y]k_Y \tag{6}$$

Für theoretische Studien ist es vorteilhaft, anstatt Milliliter Masslösung auf der Abszisse den Komplexationgrad "a" aufzutragen, der gemäss folgender Gleichung definiert ist:

$$a = \frac{C_Y}{C_M} \tag{7}$$

Kombination von (7) mit (3), (4) und (6) ergibt

$$A = C_M[k_{MY} + k_Y(a - 1)] + (k_M + k_Y - k_{MY})[M] \tag{8}$$

worin nunmehr auch [M] als Funktion von a auszudrücken ist. Dies geschieht, indem man in (5) durch Heranziehen von (3) und (4) [MY] und [Y] eliminiert und nach [M] auflöst, was folgenden Ausdruck liefert

$$[M] = \frac{[KC_M(1 - a) - 1] + \sqrt{[KC_M(1 - a) - 1]^2 + 4KC_M}}{2K} \tag{9}$$

Nur das positive Zeichen der Wurzel hat physikalische Bedeutung, was man leicht zeigen kann, da für $a = 0$ die Lösung der Gleichung sein muss $[M] = C_M$. Kombination von (8) und (9) ergibt den endgültigen Ausdruck zur Berechnung der Titrationskurve

$$A = \frac{1}{2K}\left\{2KC_M[k_{MY} + k_Y(a - 1)] + (k_M + k_Y - k_{MY})\left[KC_M(1 - a) - 1 + \sqrt{[kC_M(1 - a) - 1]^2 + 4KC_M}\right]\right\} \tag{10}$$

Die Anordnung der Glieder in (10) ist so bewerkstelligt, dass man leicht erkennt, dass bei gegebenen Absorptionkoeffizienten der Verlauf der Kurve in der Hauptsache vom Parameter KC_M abhängt.

In vielen praktischen Fällen wird der Komplexbildner farblos sein und u.U. auch das Metallion, oder aber man kann die Wellenlänge des eingestrahlten Lichtes so wählen, dass diese beiden Teilchenarten nicht absorbieren. Dann vereinfacht sich Gleichung (10) wegen $k_M = k_Y = 0$ zu

$$A = k_{MY}(C_M - [M]) \tag{11}$$

worin [M] nach (9) zu berechnen ist.

Einige Titrationskurven für wechselnde Werte von KC_M sind in Abbildung 1, 2 u. 3

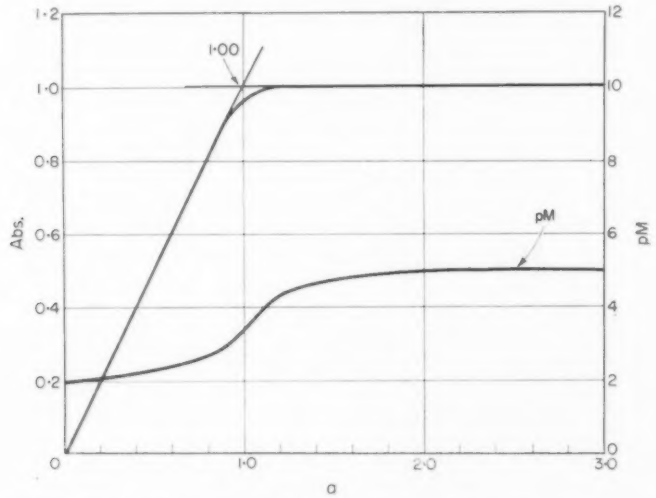

ABBILDUNG 1.—Titrationskurve für die Bestimmung eines einzelnen Metalles.
$K = 10^5$, $C_M = 10^{-2}$, $k_{MY} = 100$, $KC_M = 1000$.

gezeigt. Je niederer der Wert von KC_M desto eher weicht die Titrationskurve am Anfang von einer Geraden ab und desto später nach dem Endpunkt geht sie in eine Horizontale über. Theoretisch können äusserst geringe Werte von KC_M toleriert und immer noch brauchbare Resultate erhalten werden, wenn man die Extrapolation mit Teilen der Kurve genügend nahe dem Anfangspunkt und weit genug nach dem Endpunkte durchführt. Soweit es das Anfangsstück betrifft treten in der Praxis jedoch Schwierigkeiten auf, da die Absorptionsmessungen sehr kleine oder sehr grosse Werte aufweisen und wenig präzise sind. Für das Endstück ist zu bedenken, dass der Weg, mit a zu operierem, gleichbedeutend ist mit einer Vernachlässigung der durch den Reagenszusatz bedingten Verdünnung (siehe später).

Formel (11) gestattet es, unter Annahme plausibler Bedingungen, für KC_M eine rohen Grenzwert zu berechnen, mit dem ein noch brauchbares Resultat erhalten werden kann.

Es sei angenommen, dass die Kurvatur am Beginn so gering ist, dass zwischen dem Punkte $a = 0$ und $a = 0{,}5$ die Annäherung an eine Gerade praktisch hinreichend gegeben ist. Nach dem Äquivalenzpunkt sei die Kurve als horizontal angesehen, wenn der Anstieg zwischen $a = 2$ und $a = 2{,}5$ nur mehr 1% beträgt.

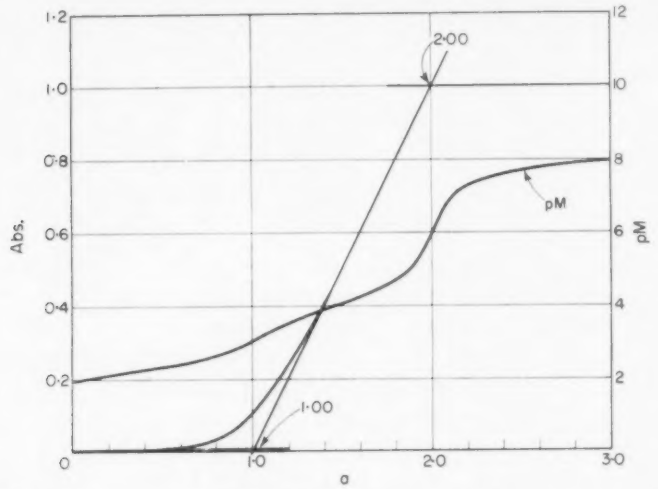

ABBILDUNG 2.—Titrationskurve für die Bestimmung eines einzelnen Metalles.
$K = 10^4$, $C_M = 10^{-2}$, $k_{MY} = 100$, $KC_M = 100$.

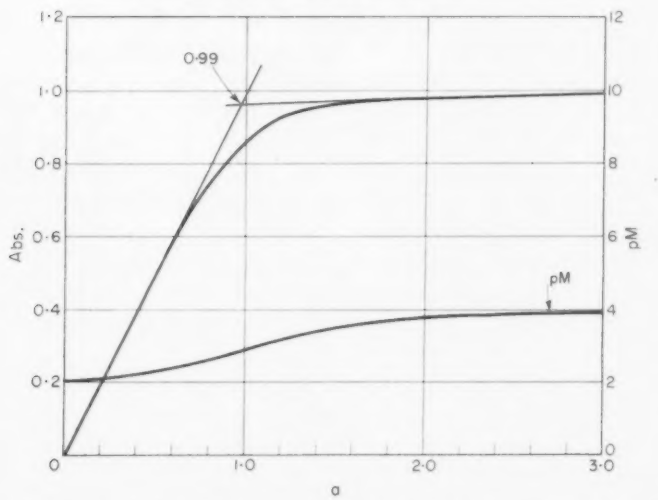

ABBILDUNG 3.—Titrationskurve für die Bestimmung eines einzelnen Metalles.
$K = 5 \times 10^3$, $C_M = 10^{-3}$, $k_{MY} = 100$, $KC_M = 50$.

Werden diese Annahmen auf den verinfachten Fall der Gleichung (11) angewandt, ergibt sich folgendes. Die erste Gerade ist gegeben durch zwei Punkte mit den Koordinaten $a = 0$, $A = 0$ und $a = 0{,}5$, $A = A_{0,5}$ Hierbei ist $A_{0,5}$ die Absorption im Punkte $a = 0{,}5$; sie kann nach (11) berechnet werden. Die zweite Gerade ist gegeben durch die beiden Punkte $a = 2$, $A = A_2$ und $a = 2{,}5$, $A = A_{2,5}$. Zusätzlich muss die Bedingung erfüllt sein, dass sich die beiden Geraden im Punkte mit den Koordinaten $a = 1$ und $A = A_1$ schneiden. Es muss nun gefunden werden, für welchen Wert von KC_M diese Bedingung erfüllt ist.

Die erste Gerade wird durch die Gleichung wiedergegeben

$$A = 2A_{0,5}a \tag{12}$$

die zweite durch

$$A = A_2 (0{,}96 + 0{,}02a) \tag{13}$$

da ja $A_{2,5} = 1{,}01\ A_2$ ist, gemäss der Annahme, dass die Zunahme der Absorption zwischen den beiden Punkten nur 1% beträgt.

Wird (12) gleich (13) und in dem resultierenden Ausdruck $a = 1$ gesetzt, so erhält man die Bedingungsgleichung

$$2A_{0,5} = 0{,}98\ A_2 \tag{14}$$

Errechnet man aus (11) die entsprechenden Werte für $A_{0,5}$ und A_2, setzt sie in (14) ein und löst nach KC_M auf, so erhält man den Wert $KC_M \simeq 50$.

Dies ist ein erstaunlich niederer Wert. Demnach kann z.B. eine 0,01 molare Metallionenlösung erfolgreich titriert werden, wenn die Stabilitätskonstante des gebildeten Komplexes nur 5 000 beträgt. Eine Kurve mit diesem Werte wurde berechnet und ist in Abbildung 3 dargestellt. Die Abbildung enhält auch die entsprechende pM-Kurve [berechnet mittels (9)]. Es ist klar zu erkennen, dass eine derartige pM-Kurve keinerlei Hoffnung auf einen auch nur einigermassen brauchbaren Endpunkt offen lässt, was immer auch die Methode seiner Festlegung sei.

Natürlich ist das durchgerechnete Beispiel nur ein Idealfall. Es wurde angenommen, dass k_{MY} genügend hoch liegt. Der Einfluss dieses Parameters spielt in der Praxis eine erhebliche Rolle. Man kann jedoch durch geeignete Wahl der Lichweglänge diese Grösse in ziemlich weiten Grenzen variieren. Wesentlich schwerwiegender ist die Idealisierung, die sich durch Verwendung von a als Abszissengrösse ergibt. In der Praxis kann a nicht verwendet werden, da ja zu seiner Berechnung die Kenntnis von C_M benötigt wird; die Ermittlung dieser Grösse jedoch ist zweck der ganzen Analyse. Für den Fall einer tatsächlichen Titration können nur Milliliter Masslösung auf der Abszisse aufgetragen werden. Um dieser Sachlage gerecht zu werden, müssen die Formeln modifiziert werden. Dies geschieht auf folgendem Wege.

C_M ist nicht mehr länger konstant, sondern ändert sich im Verlauf der Titration und muss für jede Zugabe von Masslösung gemäss folgendem Ausdruck berechnet werden:

$$C_M = \frac{C_M{}^0 V}{V + b} \tag{15}$$

Worin $C_M{}^0$ die Anfangskonzentration, V das Anfangsvolum und b das Volum an Millilitern zugesetzter Masslösung bedeuten.

C_Y lässt sich wie folgt ausdrücken

$$C_Y = \frac{mb}{V + b} \tag{16}$$

worin ausser den schon oben beschriebenen Symbolen noch m aufscheint, welches die Molarität der Masslösung bedeutet.

Die Kombination von (7), (15) und (16) ergibt nun den Ausdruck

$$a = \frac{mb}{C_M{}^0 V} \tag{17}$$

der in allen zuständigen Gleichungen einzusetzen ist. Geschieht dies, so erhält man

für die Berechnung der Titrationskurve folgende Gleichung

$$A = \frac{C_M{}^0 V}{V + b}\left[k_{MY} + k_Y\left(\frac{mb}{C_M{}^0 V} - 1\right)\right] + (k_M + k_Y - k_{MY})[M] \qquad (18)$$

woring [M] nach folgender Formel zu berechnen ist:

$$[M] = \frac{-\left[KC_M{}^0 \frac{V}{V+b}\left(\frac{mb}{C_M{}^0 V} - 1\right) + 1\right] + \sqrt{\left[KC_M{}^0 \frac{V}{V+b}\left(\frac{mb}{C_M{}^0 V} - 1\right) + 1\right]^2 + 4KC_M{}^0 \frac{V}{V+b}}}{2K} \qquad (19)$$

Für den vereinfachten Fall, dass nur die Spezie MY absorbiert ergibt sich

$$A = k_{MY}\left(\frac{C_M{}^0 V}{V+b} - [M]\right) \qquad (20)$$

worin [M] ebenfalls durch (19) ausgedrückt werden muss.

Die Gleichung ist ungleich komplizierter als (11); sie geht für die Bedingung $V \gg b$ in (11) über.

Ein Versuch, einen Mindestwert für $KC_M{}^0$ zu berechnen, scheitert daran, dass im Zuge der Rechnung Gleichungen von so hoher Ordnung auftreten, dass ihre Lösung algebraisch nicht mehr möglich ist. Es ist daher einfacher vom Falle der vernachlässigten Verdünnung (operieren mit a) einen plausiblen Schluss zu ziehen und anzunehmen, dass ein $KC_M{}^0$-Wert von etwa 200–500 noch gute Resultate liefern wird und diesen Schluss dann experimentell zu prüfen.

Wie schon oben dargelegt, wird es mit fallendem KC_M-Wert nötig, die Extrapolation der ersten Geraden so nahe am Anfangspunkte zu beginnen als nur möglich. Für die zweite Linie wird man recht weit hinter den Äquivalenzpunkt gehen. Letzteres jedoch bedeutet Zugabe einer beträchtlichen Menge an Masslösung, selbst wenn diese in recht hoher Konzentration vorliegt. Im allgemeinen kann man bei diesen Arten von Titrationen der Verdünnung Rechnung tragen, indem man eine Korrektur anbringt. Dies geschieht durch Multiplizieren von A mit dem Faktor $(V + b)/V$. Wird jedoch ein sehr schwacher Komplex als Grundlage der Titration herangezogen, so muss bedacht werden, dass die Verdünnung in zwei verschiedenen Richtungen wirkt. Einmal wird die abgelesene Absorption geringer sein als Folge einer lediglichen Verdünnung der "Farbe" der Lösung. Anbringen der Korrektur trägt diesem Umstande völlig Rechnung. Zum anderen wird jedoch in der verdünnteren Lösung der Komplex stärker dissoziieren. Diese Verschiebung des Gleichgewichtes wird natürlich nicht korrigiert.

Ausser in einer sehr ungünstigen Situation ist jedoch dieser Faktor nicht von zu grossem Einfluss, wie man aus Abbildung 4 erkennen kann. Ohne Korrektur für die Verdünnung ist der gefundene Wert wesentlich zu nieder (9,25 statt 10,00). Nach Korrektur der Kurve ergibt sich 10,19 was nur um 2% zu hoch ist. Die pM-Kurve ist für eine Endpunktsfestlegung, nach welcher Methode auch immer vorgegangen wird, absolut unbrauchbar.

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Deshalb ergibt sich hier also im allgemeinen die Forderung, mit möglichst konzentrierten Masslösungen zu arbeiten, nicht nur aus dem sonst üblichen Grunde, dass das Anbringen der Korrektur zeitraubend und umständlich ist, sondern vielmehr, weil die Korrektur die Verzerrung der Kurve einfach nicht völlig beheben kann. Doch kann diese Kompensation nicht beliebig weit getrieben werden. Einmal gebietet die Löslichkeit des Titrationsmittels ein Halt, zum anderen benötigt man feiner geteilte Büretten mit kleinerem Fassungsraum, was ebenfalls begrenzt ist.

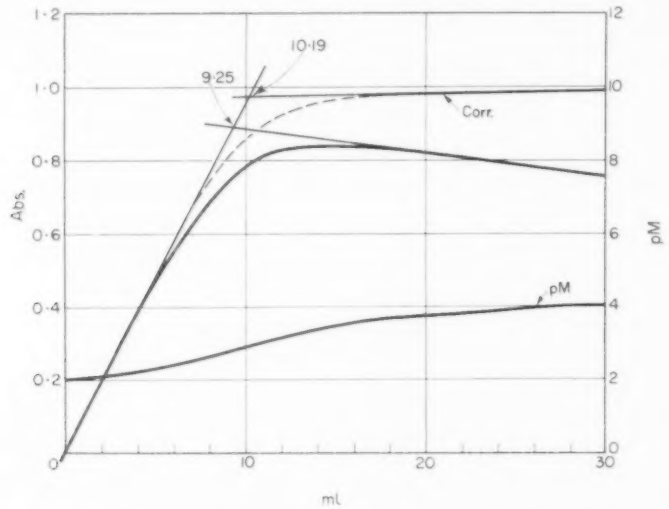

ABBILDUNG 4.—Titrationskurve für die Bestimmung eines einzelnen Metalles ohne und mit Berücksichtigung der Verdünnung durch das Titrationsmittel.
$K = 5 \times 10^3$, $C_M^0 = 10^{-2}$, $k_{MY} = 100$, $KC_M = 50$, V = 100 ml, m = 10^{-1}.

(B) *Chelometrische Titration von zwei Metallen nacheinander in derselben Lösung, ohne Verwendung eines Indikators*

Wenn zwei Metalle zu titrieren sind, werden die mathematischen Ableitungen wesentlich komplizierter, weshalb hier nur auf die Behandlung des Falles eingegangen wird, wo die Verdünnung vernachlässigt werden kann.

Die Stabilitätskonstanten der Komplexe der beiden zu titrierenden Metalle M und N sind gegeben durch

$$K_M = \frac{[MY]}{[M][Y]} \tag{21}$$

$$K_N = \frac{[NY]}{[N][Y]} \tag{22}$$

In jeder Phase der Titration müssend die folgenden drei Gleichungen erfüllt sein

$$C_M = [M] + [MY] \tag{23}$$

$$C_N = [N] + [NY] \tag{24}$$

$$C_Y = [Y] + [MY] + [NY] \tag{25}$$

Es ist offenkundig, dass die Möglichkeit, beide Metall in derselben Lösung *hintereinander* zu titrieren, einmal vom Unterschied in den Stabilitätskonstanten der

Komplexe abhängt. Um diesem Umstande Rechnung zu tragen, wird der Quotient "Q" eingeführt, definiert gemäss

$$Q = \frac{K_M}{K_N} \tag{26}$$

Zum anderen wird die Titration beider Metalle nur möglich sein, wenn die zu titrierenden Spezies und/oder die gebildeten Komplexe optisch differenziert werden können, sodass zwei klar unterscheidbare Knicke in der Titrationskurve (die nun drei Äste aufweisen muss) auftreten. Ob und in welchem Masse dies der Fall ist, hängt von den k-Werten der beteiligten Teilchenarten ab, denn Gleichung (2) ist ja auch für diesen Fall gültig.

Unter Verwendung der einschlägigen Gleichungen lässt sich der Ausdruck zur Berechnung der Titrationskurve wie folgt ableiten.

In Gleichung (26) werden alle Ausdrücke so ersetzt, dass nur mehr [M] als Variable aufscheint. Hierzu erhält man aus (23) $[MY] = C_M - [M]$. Aus (21) errechnet sich $[Y] = (C_M - [M])/[M]K_M$. Dies in Kombination mit (24) und (25) ergibt $[NY] = C_Y - (C_M - [M]) - (C_M - [M])/[M]K_M$, beziehungsweise $[N] = C_N - C_Y + (C_M - [M]) + (C_M - [M])/[M]K_M$ Einsetzen in (26) führt schliesslich zu

$$Q = \frac{C_M - [M]}{[M]} \times \frac{C_N - C_Y + (C_M - [M]) + \dfrac{C_M - [M]}{[M]K_M}}{C_Y - (C_M - [M]) - \dfrac{C_M - [M]}{[M]K_M}} \tag{27}$$

Ein Versuch, [M] als Funktion von C_Y auszudrücken, führt zu einer Gleichung dritten Grades in [M], was für praktisches Arbeiten unbrauchbar ist. Um die Titrationskurve zu berechnen löst man daher nach C_Y auf und berechnet umgekehrt den für verschiedene [M]-Werte sich ergebenden Betrag an Titrationsmittel und gelangt so zum gewünschten Ziele. Die so erhaltene Formel lautet

$$C_Y = \frac{C_M - [M]}{[M]}\left(\frac{C_N}{Q + \dfrac{C_M - [M]}{[M]}} + [M] + \frac{1}{K_M}\right) \tag{28}$$

Führt man weiters noch den Titrationsgrad "a" gemäss (7) definiert ein, so resultiert

$$a = \frac{1}{C_M}\frac{C_M - [M]}{[M]}\left(\frac{C_N}{Q + \dfrac{C_M - [M]}{[M]}} + [M] + \frac{1}{K_M}\right) \tag{29}$$

Zur Berechnung der Absorption seien die folgenden, zum Teil vereinfachenden Annahmen gemacht. Metall M bilde den stabileren Komplex, d.h. es wird also zuerst titriert. Die einzige, bei der gewählten Wellenlänge absorbierende Spezie ist NY. Dann ergibt sich unter Anwendung von (2) und entsprechendem Ersatz von [NY]

$$A = k_{NY}[NY] = k_{NY}\left[QC_M - (C_M - [M]) - \frac{C_M - [M]}{[M]K_M}\right] \tag{30}$$

Verschiedene [M]-Werte werden angenommen und mittels (29) wird a berechnet; die so erhaltenen Werte für a sowie die korrespondierenden [M]-Werte werden in (30)

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eingesetzt und liefern die Absorptionen, sodass die Titrationskurve konstruiert werden kann. Kurven für verschiedene Werte von Q und K_M sind für äquimolare Mischungen der beiden Metalle berechnet worden und in den Abbildungen 5–9 dargestellt.

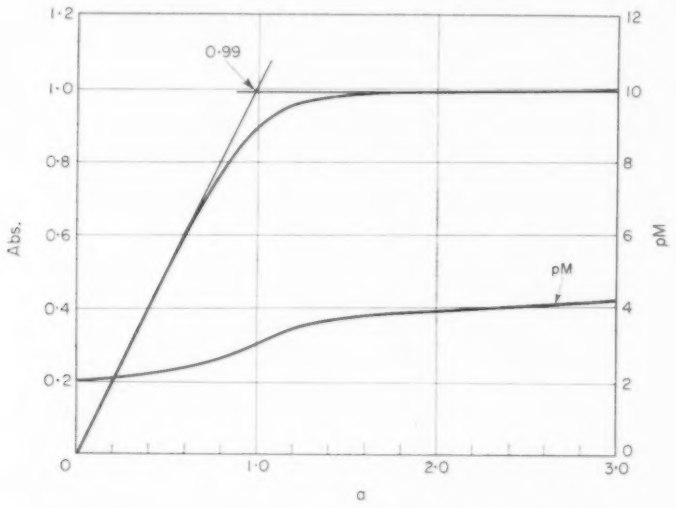

ABBILDUNG 5.—Titrationskurve zur Bestimmung von zwei Metallen.
$K_M = 10^{10}$, $K_N = 10^7$, Q = 1000, $C_M = C_N = 10^{-2}$, $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

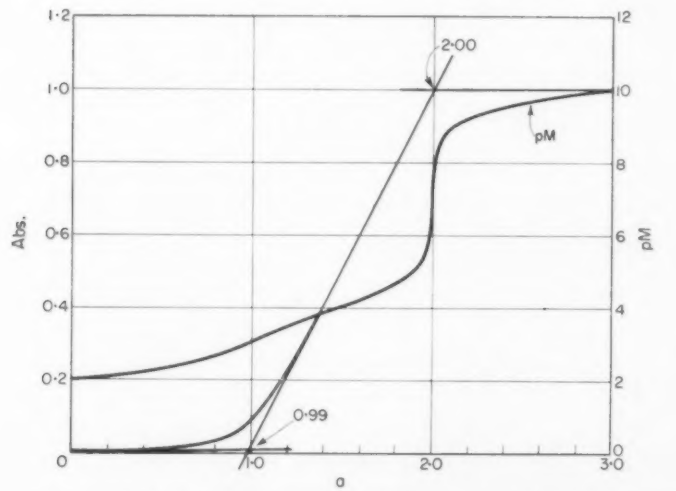

ABBILDUNG 6.—Titrationskurve zur Bestimmung von zwei Metallen.
$K_M = 10^{10}$, $K_N = 10^8$, Q = 100, $C_M = C_N = 10^{-2}$, $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

Zum Vergleich sind auch die entsprechenden pM-Kurven eingezeichnet. Auch hier zeigt sich wieder deutlich die Überlegenheit der photometrischen Titration.

Die Verhältnisse liegen hier jedoch wesentlich komplizierter. Der Kurvenverlauf ist einmal abhängig von Q. Das heisst, je grösser Q ist, desto besser lassen sich die beiden Metall getrennt erfassen. Zum anderen spielt aber auch die Grösse von K_M

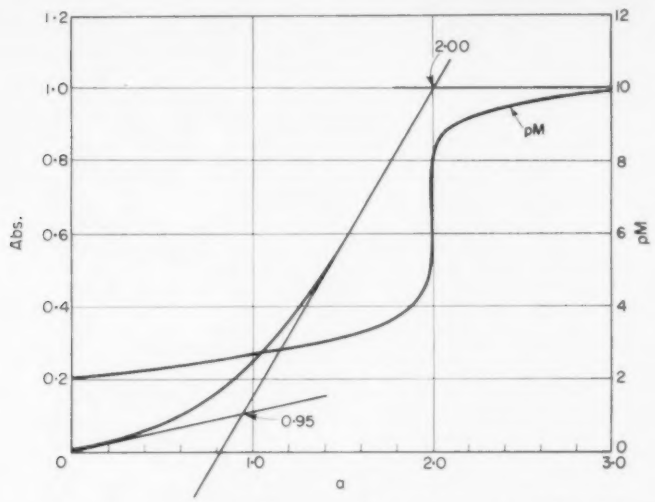

ABBILDUNG 7.—Titrationskurve zur Bestimmung von zwei Metallen.
$K_M = 10^{10}$, $K_N = 10^9$, Q = 10, $C_M = C_N = 10^{-2}$, $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

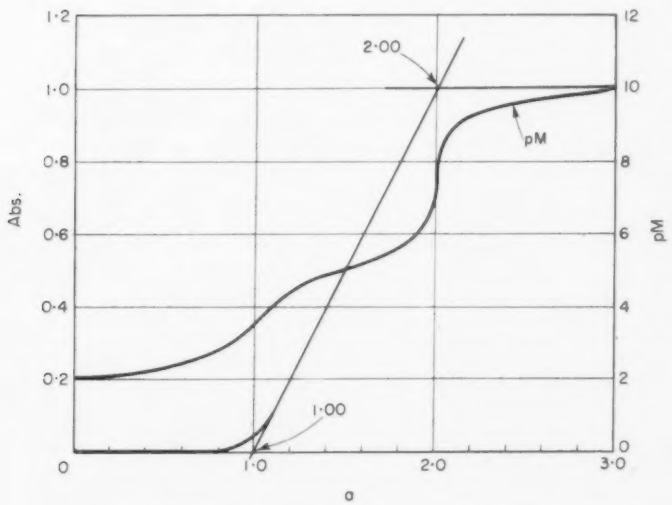

ABBILDUNG 8.—Titrationskurve zur Bestimmung von zwei Metallen.
$K_M = 10^8$, $K_N = 10^6$ Q = 100, $C_M = C_N = 10^{-2}$ $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

eine entscheidende Rolle. Ist der Wert dieses Parameters klein (absolut und noch wesentlicher im Vergleich zu C_M) so wird, wie zu erwarten, die Lokalisierung des ersten Endpunktes schwierig.

Es ergibt sich für äquimolare Gemische der immerhin erstaunlich niedere, ungefähre Mindestwert für Q (bei annehmbar hohem K_M) von etwa 100. Auch dies ist ein unter Idealbedingungen abgeleiteter Wert und entsprechende Modifikationen sind nötig, wenn die Konzentrations-verhältnisse der beiden Metalle und die *k*-Werte ungünstig liegen. Aber auch dann ist die photometrische Titration der visuellen oder anderen, ohne Extrapolation arbeitenden Titrationen deutlich überlegen.

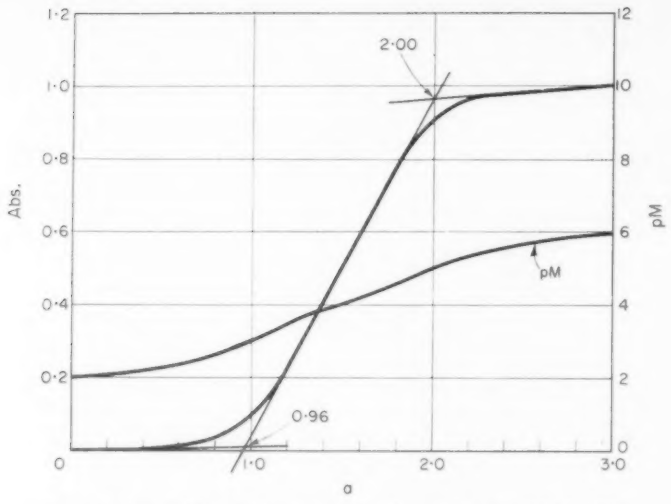

ABBILDUNG 9.—Titrationskurve zur Bestimmung von zwei Metallen.
$K_M = 10^6$, $K_N = 10^4$ Q = 100. $C_M = C_N = 10^{-2}$ $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

Wird die Verdünnung nicht vernachlässigt, so müssen wie im einfachen Falle der Titration eines einzelnen Metalles die Konzentrationen der drei Reaktanten durch Ausdrücke gemäss (15) und (16) ersetzt werden. Dies führt zu einer Gleichung, die zwar algebraisch gehandhabt werden kann, wobei aber der Rechenaufwand so gross ist, dass der Wert der gewonnenen Erkenntnisse mit der hineingesteckten Arbeit kaum mehr vergleichbar ist. Man muss bedenken, dass die interessantesten Fälle jene sind, bei denen man sich nahe den tolerierbaren Grenzen befindet. Unter diesen Umständen spielen kleine Änderungen in der Konzentration und vor allem in den scheinbaren Stabilitätskonstanten eine recht grosse Rolle. Die scheinbaren Stabilitätskonstanten können in vielen Fällen nicht berechnet werden. In einem tatsächlichen Titrationsgemisch ist die ionale Stärke kaum gleich der, für welche die absoluten Konstanten bekannt sind. Anwesenheit zusätzlicher auch nur schwacher Komplexbildner verursacht weitere Änderungen, die oftmals mangels der nötigen Daten nicht rechnerisch erfasst werden können. Alle Parameter unterliegen während der Titration kleinen Änderungen. Diese und noch andere Einflüsse, wie z.B. das auch nur teilweise Auftreten von sauren und Hydroxokomplexen, machen eine exakte Berechnung schwierigm, wenn nicht überhaupt unmöglich. Es ist wesentlich einfacher für ein im fraglichen Bereich liegendes System, anstatt es durchzurechnen, die Prüfung im Experiment heranzuziehen.

Nichtsdestoweniger aber sind die abgeleiteten Formel für rohe Abschätzungen von grossem Wert. Vor allem aber ermutigen sie Systeme zu untersuchen, die man ansonsten als aussichtslos nie in näheren Betracht gezogen hätte.

(C) *Betrachtungen über einige weitere Möglichkeiten*

Die sich aus den obigen, theoretischen Betrachtungen ergebenden Möglichkeiten können, soweit es praktische Anwendungen betrifft, noch vorteilhaft erweitert werden, indem man die beschriebenen Methoden mit anderen kombiniert. Das lässt sich z.B. am System Kupfer-Nickel zeigen. Wie schon in früher erschienenen Arbeiten gezeigt

wurde,[20,21] kann Kupfer sehr leicht und störungsfrei neben Nickel (und anderen Metallionen) bestimmt werden, wenn man mit TRIEN bei pH 5–6 photometrisch ohne Indicator titriert. Nickel anschliessend durch weitere Zugabe von TRIEN zu erfassen ist nicht gut möglich, da die durch das Nickel hervorgerufenen Absorptionsänderungen (auch in anderen pH-Bereichen) zu gering sind. Wohl aber kann man durch einfache Zugabe von Ammoniak und Murexid Bedingungen schaffen, unter denen photometrisch ein scharfer Endpunkt resultiert. Dergestalt können Kupfer und Nickel in derselben Lösung hintereinander titriert werden. Ähnliche Möglichkeiten sind für weitere Systeme in Ausarbeitung und über die Resultate wird später berichtet werden.

Man kann weiters zwei Metalle mit zwei verschiedenen Indicatoren und wenn nötig zwei verschiedenen Masslösungen hintereinander titrieren, was visuell praktisch unmöglich ist, da in fast allen Fällen der erste Indicator das Erkennen des zweiten Umschlages für das menschliche Auge unmöglich macht. Die Photozelle des Titrationsgerätes jedoch kann sehr wohl die verschiedenen Änderungen auseinanderhalten.

Die oben abgeleitete Tatsache, dass man zwei Metalle getrennt titrieren kann, auch wenn der Unterschied in den Stabilitätskonstanten nur relativ gering ist, öffnet die Möglichkeit zum Einsatz neuer Maskierungsmittel. Es können nämlich nunmehr als Maskierungsmittel Komplexbildner herangezogen werden, bei denen die Stabilität des Maskierungskomplexes zu gering ist, um eine visuelle Titration zu ermöglichen, da der erzielten Unterschied in der Stabilität der Titrationskomplexe nicht genügend gross wird.

Die bisher genannten Möglichkeiten, sowie deren Kombination und noch weitere mehr können nutzbringend verwendet werden, um dem Selektivitätsproblem chelometrischer Titrationen erfolgreich näher zu treten. Über ihre praktische Anwendung wird beim Studium verschiedener Systeme in folgenden Mitteilungen dieser Reihe berichtet werden.

Die vorliegende Arbeit wurde mit Unterstützung der National Science Foundation durchgeführt.

Summary—The characteristics of chelatometric titrations with a photometric end-point without an indicator are discussed, and formulae are derived for the calculation of the titration curves. It is shown that in titrating a single metal a considerably smaller stability of the titration complex can be tolerated than in other methods of fixing the end-point which do not depend on extrapolation. For the titration of two metals in the same solution, in succession, a difference in the stability constants of a factor of about 100 to 200 is sufficient. The possibilities of using the method in combination with other end-point methods are discussed, and problems of selectivity are considered.

Résumé—L'auteur discute des caractéristiques des titrages complexométriques avec point équivalent déterminé par photométrie, sans indicateur; les formules des courbes de titrages sont établies L'auteur montre que, pour titrer un métal seul, une faible stabilité du complexe de titrage peut être tolérée, de même que dans d'autres méthodes de fixation du point équivalent qui ne dépendent pas de l'extrapolation. Pour le titrage successif de deux métaux dans la même solution, une différence des constantes de stabilité d'un facteur 100 à 200 environ est suffisante. Les possibilités d'utiliser cette méthode combinée avec d'autres méthodes de détection du point équivalent sont discutées, les problèmes de sélectivité sont considérés.

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THE ANION-EXCHANGE SEPARATION OF TECHNETIUM, RHENIUM AND MANGANESE

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Summary—An anion-exchange method for the separation of technetium, rhenium and manganese is outlined. After sorption on the resin column, manganese is first eluted with hydrochloric acid, rhenium with ammonium thiocyanate in hydrochloric acid, and technetium by means of nitric acid. In the eluates rhenium is determined colorimetrically and technetium radiochemically. As little as 10 μg of technetium in the form of potassium pertechnetate can be separated from 15 mg of manganese as potassium permanganate and 0·8 mg of rhenium in the form of potassium perrhenate.

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IN 1955, Gerlit,[1] discussing the chemical properties of technetium, remarked on the lack of analytical procedures for the element. Since that date the position has improved somewhat and publications have appeared dealing with a number of aspects of the analytical chemistry of the element.[2] One aspect of the analytical chemistry which, however, appears to have had scant attention is that associated with the ion-exchange behaviour of the element, particularly in relation to the other elements of Group VIIa of the Periodic Classification, *i.e.* manganese and rhenium.

The first ion-exchange study of technetium and rhenium was carried out by Atteberry and Boyd[3] using ion-exchange resin Dowex 2. Both elements in this work were sorbed on a resin column 0·72 cm^2 × 51 cm and eluted at a flow rate of 1·7 ml/min with ammonium sulphate and thiocyanate at pH 8·3–8·5. By this procedure a clear separation of rhenium and technetium was not obtained. The authors further state that as manganese in the form of permanganate reacts with the resin, no experiments were carried out with all three elements.

The ion-exchange separation of technetium and molybdenum has also been investigated by Huffman, Oswalt and Williams,[4] and the separation of technetium and rhenium on resin Dowex 1, using perchloric acid as eluent was studied by Sen Sarma *et al.*[5] These latter workers found that the separation was not clean and showed a residual tailing effect which could not be eliminated. Other attempts at the separation of technetium and rhenium have been carried out,[6] but as pointed out,[7] they suffer from shortcomings such as low separation factors, low yields and failure at trace levels.

This paper describes the results of investigations carried out on the anion-exchange separation of manganese, technetium and rhenium.

EXPERIMENTAL

Reagents and apparatus

Amberlite IRA 400 *resin* was used. After grinding in a mortar and sieving, particles in the range 72–100 B.S.S. mesh were washed thoroughly with 2*N* nitric acid and then converted into the chloride form.

Potassium pertechnetate: An aqueous solution containing 10 μg/0·1 ml was used.
Potassium perrhenate: An aqueous solution containing 2·5 mg/ml. was used.
Potassium permanganate: An aqueous solution containing 10 mg/ml. was used.

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4π Gas flow counter: For counting the soft β particles (0·29 MeV) emitted by ^{99}Tc, a 4π Gas Flow Counter (Labgear Type D4126) was used. As a check, some experiments were carried out with a Scintillation Counter (Ekco Ltd., Type N664A).

INVESTIGATIONS

Numerous attempts were made to separate rhenium and technetium by sorbing them on the resin as pertechnetate and perrhenate and eluting with different eluents. Elution with 0·1*N* perchloric acid[5] showed some success, but elution curves overlapped. Attempts using mixed solvents such as alcohol–water and perchloric acid or acetone–water and perchloric acid gave elution curves inferior to water and perchloric acid alone. In the report to the International Conference on the Peaceful Uses of Atomic Energy,[1] Gerlit states that pertechnetate in strong hydrochloric acid is reduced to the 4-valent state. An attempt was made to use this as a basis of separation of technetium and rhenium, but without success. Complexing eluents were next investigated, and of these the most successful were potassium xanthate and ammonium thiocyanate. The former appeared to separate the two elements, but as the reagent exerts a very strong quenching effect radiochemically, measurement of technetium was never certain and the method was abandoned. The most satisfactory separation was achieved with ammonium thiocyanate.

Separation of Mn, Tc and Re using ammonium thiocyanate

(*a*) *Preparation of the test sample.* Prepare the elements for separation by dissolving them, in the permanganate, pertechnetate and perrhenate forms, in 5 ml of water. Acidify with hydrochloric acid until the normality is 0·1–0·3 in hydrochloric acid. Add Perhydrol to reduce permanganate to manganese chloride and remove excess Perhydrol by heating. The test sample is now ready for transference to the ion-exchange column.

(*b*) *Operation of the column.* Transfer the prepared test sample to a column of Amberlite IRA 400 resin of dimensions 0·2 cm^2 × 2·5–3 cm. Wash out the vessel containing the test sample with approximately 3 ml of 0·1–0·2*N* hydrochloric acid. When the level of the liquid reaches the top of the resin, using a flow rate of 1 ml/15 min, wash with 0·1–0·2*N* hydrochloric acid at a rate of 1 ml/6 min to elute manganese. Manganese in the reduced form is not sorbed on the resin, and complete removal is effected in 20 ml of eluate.

To separate rhenium and technetium, add 5% ammonium thiocyanate in 0·1–0·2*N* hydrochloric acid to the column and elute at a rate of 1 ml/15 min. Under the conditions outlined all of the rhenium is eluted in 15–20 ml of solution (Fig. 1).

Wash the column with 10 ml of water to remove ammonium thiocyanate and follow with 20 ml of 0·1*N* nitric acid at a flow rate of 1 ml/10 min to remove the CNS^- remaining in the column (*cf.* Note 4). Change the concentration of nitric acid to 4*N* and elute at a flow rate of 1 ml/15 min to remove technetium from the column (Fig. 1).

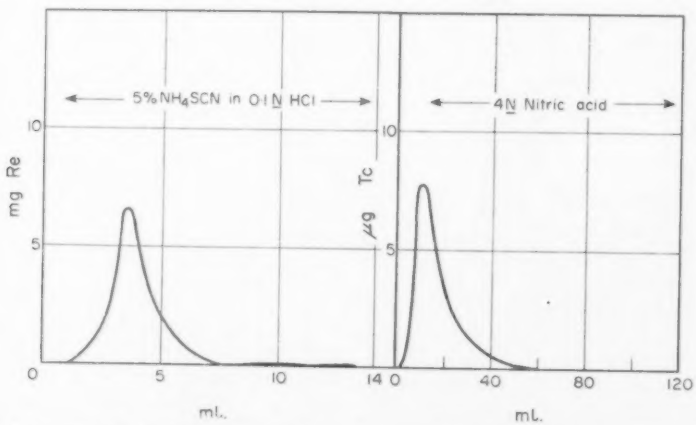

Fig. 1.—Separation of rhenium and technetium. Column: 2·5 cm × 0·2 cm^2. Amberlite IRA 400, mesh 72-100. Flow rate: 1 ml/15 min.

Notes

1. After 20 ml of 0·1–0·2*N* hydrochloric acid had passed through the column to elute manganese, no positive test for the element was ever found in subsequent eluates.
2. Technetium was never detected in the manganese or rhenium eluates.
3. When technetium is sorbed on the column as pertechnetate, a small fraction (0·1–0·2%) always passes through. This has also been observed by other workers.[4]
4. When 0·1*N* nitric acid is used to elute technetium, it reacts with the CNS^- remaining in the column, and a ring of NO_2 moves down the column. If the nitric acid is passed down the column at a fast rate, the reaction is vigorous and bubbles are produced. With this treatment usually no technetium is eluted, but on occasions 0·05–0·1% was washed out.
5. With 40 ml of 4*N* nitric acid, more than 90% of technetium is removed from the column (Fig. 1). For complete removal 200 ml of eluent is required.
6. The resin particle size has an effect on the elution rate of technetium. For resin particle sizes in the range 52–72 B.S.S., extraction was slower and incomplete. At particle size below 52 B.S.S. very large amounts of nitric acid were required to remove technetium, and removal was incomplete. Retention of technetium by the column was also observed if the same resin column was used too often.
7. Elution of the three elements requires a total time of about 24 hr.

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DETERMINATION OF TECHNETIUM AND RHENIUM

1. *Technetium*

Numerous experiments were carried out to investigate possible ways of determining technetium after its removal form the ion-exchange column. A difficulty in the determination is that the element is volatile in solutions of sulphuric and perchloric acid. Chloride is also a strong quenching agent in scintillation counting. Mounting of the sample for counting was also found important, if reproducible results were to be obtained. The most satisfactory procedure using the proportional counter is outlined below.

Procedure: Evaporate the nitric acid solution from the column, containing technetium, under an infrared lamp until the volume is about 0·5 ml. The temperature of the solution should always be less than 90°.

Dilute the volume to 1 ml in a graduated flask and deliver 0·05 ml of this solution to a piece of filter paper, ensuring that the diameter of the spot is never greater than about 1 cm.

Place in the proportional counter and measure.

Notes

1. Under the conditions outlined reproducibility was good.
2. With the proportional counter a background of 90–100 counts/100 sec was usually obtained and 0·5 μg Tc in 0·05 ml gave a count of around 4000/100 sec.
3. Many salts quench counting, and their presence must be avoided. In the procedure above a little quenching is observed by, it is thought, solubles extracted from the resin by the nitric acid. This was determined and found to be less than 10%.

An attempt was made to determine technetium spectrophotometrically in the nitric acid eluate. Technetium as pertechnetate absorbs at very short wavelength. Rulfs and Meinke[8] determined the absorption spectrum of pertechnetate in hydrochloric acid and found two absorption peaks at 290 mμ and 247 mμ. This was later confirmed.[9] In the present work, since it was found that nitric acid absorbs in the same region of the ultraviolet as pertechnetate, it was the intention to expel nitric acid and re-dissolve in hydrochloric acid. The absorption spectrum of potassium pertechnetate in 0·1*N* hydrochloric against a 0·1*N* hydrochloric acid blank was determined. This shows a clear absorption peak at 206 mμ. No peaks at 247 or 290 mμ were obtained. When, however, attempts were made to use this method for the determination of technetium, difficulties were encountered. On evaporation of nitric acid, traces always remained which caused fluctuations in the results. Stronger heating to remove the traces of nitric acid led to the danger of loss of some technetium. Using this method, the error was around 20%. The thiocyanate method recommended by Crouthamel[10] was also investigated, but for the small quantities of technetium involved was found to be unsatisfactory.

TABLE 1.

No.	Rhenium		Technetium		Manganese	
	Given	Found	Given	Found	Given	Found
1	1·25	1·00	0·01	0·01		
2	2·5	2·25	0·02	0·02		
3	2·5	2·38	0·015	0·013(6)		
4	1·25	1·4	0·02	0·017		
5	1·25	1·25	0·01	0·009(2)		
6	0·125	0·125	0·03	0·028(5)		
7	0·125	0·15	0·15	0·13		
8	2·5	2·88	0·2	0·22		
9	1·25	1·25	0·01	0·01	15·0	Not
10	1·25	1·25	0·01	0·009(5)	15·0	Determined

2. *Rhenium*

Rhenium is eluted from the ion-exchanger with 5% ammonium thiocyanate in hydrochloric acid. It was found to be a simple matter to determine the rhenium in this eluate colorimetrically using the method of Geilmann *et al.*[11] In this method, an acid solution of perrhenate, on treatment with thiocyanate and stannous chloride, exhibits a yellowish colour which has been attributed to the formation of $ReO(CNS)_4^-$. At room temperature, maximum colour development takes place within 10 min, and there is no significant change in 30 min. Employing standard conditions, results were found to be reproducible.

Synthetic mixtures

As a final test on the proposed method, some "unknown" mixtures were analysed by one of us (M.P.). The results are shown in Table I. All quantities are expressed in mg.

Samples 9 and 10 contained 15 mg of manganese, which was removed according to the proposed scheme, but not determined.

In all the samples rhenium was present as perrhenate and technetium as pertechnetate.

In samples 3 and 4 an "aged" resin which had been used many times was employed. (*cf.* Note 6 under *Operation of the Column*). To achieve the values, No. 3–0·013(6) mg (error −9%), No. 4–0·017 mg error −15%), 60 ml of 4*N* nitric acid were required. With 20 ml of 4*N* nitric acid a considerable quantity of technetium was retained by the column.

Acknowledgement—One of the authors (M. Pirs) wishes to thank the International Atomic Energy Agency for the grant which made this work possible.

Zusammenfassung—Eine Ionenaustauscher-Methode zur Trennung von Technetium, Rhenium und Mangan wird beschrieben. Nach Sorption an der Säule wird zuerst Mangan mit verdünnter Salzsäure eluiert, dann Rhenium mit Ammoniumthiocyanat in Salzsäure und zuletzt Technetium mit Salpetersäure. In den Eluaten werden Rhenium photometrisch und Technetium radiochemisch bestimmt. 10 μg Technetium als Kaliumpertechnatat können von 15 mg Mangan (als Kaliumpermanganat) und 0·8 mg Rhenium (als Kaliumperrhenat) getrennt werden.

Résumé—Les auteurs donnent un aperçu d'une méthode de séparation du technétium, du rhénium et du manganèse per échange d'ions. Après fixation sur une colonne de résine, le manganèse est élué

en premier par de l'acide chlorhydrique, le rhénium par du thiocyanate d'ammonium dans l'acide chlorhydrique et le technétium par de l'acide nitrique. Dans les solutions éluées, le rhénium est dosé par colorimétrie, et le technétium par radiochimie. 10 μg de technétium sous forme de pertechnétate de potassium peuvent être séparés de 15 mg de manganèse à l'état de permanganate de potassium et de 0·8 mg de rhénium à l'état de perrhénate de potassium.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—IV

INVESTIGATION OF A TARTRATE COMPLEX CONTAINING BOTH COPPER AND ALUMINIUM

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Summary—The theory of complementary tri-stimulus colorimetry has been extended and applied to the study of equilibria. A mixed complex containing copper, aluminium and tartrate has been studied. The mixed complex is more stable than the tartrate complexes of the individual metals and is even formed in solutions containing more tartrate than is necessary to form the single complexes. Formation of the mixed complex is slow, as is its reaction with other complex-forming substances, and it is accompanied by the release of hydroxyl ions. The pH range of existence of the mixed complex has been determined and its composition has been investigated.

SEVERAL years ago triethylenetetramine (trien) was studied as a chelating titrant in the photometric titration of copper[II].[1,2] In the course of this investigation an unexpected time effect was observed when copper was titrated at pH 8 in tartrate solution in the presence of aluminium ion. The concentration of tartrate was maintained sufficiently high to assure its complexation with both copper and aluminium separately. The inference from that effect (which is most pronounced at about pH 8 and which vanishes gradually when the pH is either lowered or raised) was that a complex species is formed which contains tartrate and both metal ions. This mixed complex must have a higher stability than the individual tartrate complexes of aluminium and of copper. Some changes in the absorbance curve of a copper tartrate solution after the addition of aluminium ion were observed, thus providing further evidence for the existence of such a mixed complex.

Both the formation of the mixed complex and its reaction with other complex forming agents are slow. If a copper tartrate solution is mixed with an aluminium tartrate solution, both buffered to about pH 8, the photometric titration of copper with trien is possible if it is started immediately and performed quickly. If the mixed solution is allowed to stand overnight or if it is heated to boiling and cooled, the galvanometer needle creeps after each addition of trien and the titration is rendered practically impossible. The rate at which the copper is transferred from the mixed copper–aluminium–tartrate complex to the trien complex can be followed by adding an excess of trien and observing the absorbance as a function of time. A plot of such time curves is shown in Fig. 11.

It has been found that citrate behaves in a similar fashion. Further investigation has shown that chromium[III] also behaves in the same manner as aluminium. In this case, the time effect is even more pronounced and it seems that only a portion of the copper is ever released from the mixed complex; some is held permanently and it is not transferred to the trien complex even after standing for several hr. More research is

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needed in this direction. An analogous mixed complex, containing uranium^{VI}, aluminium and citrate in a molar ratio of 1:1:2 has been described by Booman and Holbroock.[3]

Complementary tri-stimulus colorimetry has been developed and several publications[4–8] have shown the value of this approach in the investigation of equilibria. One of the main advantages lies in the possibility of utilising many wavelengths in a particular region rather than one, as is usual in other approaches where, generally, only the absorption maxima are employed to derive conclusions. Furthermore, some of the parameters in complementary tri-stimulus colorimetry are independent of the analytical concentration of the colorant species involved, thus offering distinct advantages. It seemed worthwhile, therefore, to apply this approach to the investigation of the mixed copper–aluminium–tartrate complex. No references could be found in the literature to the existence of such a complex other than the two mentioned above.[2,3] Of course, a great number of mixed complexes are known in which more than one metal is co-ordinated with a multidentate ligand but the co-ordination of two metals within one complex species, in the presence of a ligand concentration which is more than sufficient to complex both metals separately, appears quite unusual.

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From the viewpoint of analytical chemistry, the investigation seems important because of the interferences caused by aluminium in the above mentioned determination of copper. Furthermore, this time effect may offer possibilities for a kinetic masking of copper, provided, of course, that analogous complexes with other metals such as nickel or cobalt do not exhibit the same behaviour.

Such mixed complex formation was probably not discovered earlier because it does not manifest itself strongly in the visible region of the spectrum. Only a very slight change in colour occurs when moderate amounts of aluminium tartrate are added to a copper tartrate solution. Furthermore, this change occurs slowly and then only within a limited pH range.

The main purpose of the present paper is to extend the theoretical background of complementary tri-stimulus colorimetry in its application without relation to the human eye, and to establish unambiguously the existence of the peculiar mixed complex. To reach definite conclusions about composition, mechanism of formation, stability, *etc.* of the mixed complex is difficult because so little is known about the tartrate complexes of copper and even less about those of aluminium. The existing literature is frequently contradictory and many of the relevant papers are available as abstracts only. Hence, some investigations of the copper tartrate complex alone have been included.

In the preceding paper of this series,[8] it was stated that the occurrence of a straight line in a u–v plot is a necessary but insufficient condition for the presence of an equilibrium which involves only two absorbing species (*i.e.* absorbing in the selected region of the spectrum); this is the case with most acid-base indicators. From an understanding of the basis of complementary tri-stimulus colorimetry, this statement might be treated as self-evident. Nevertheless, in the following paragraph, a mathematical proof will be given because it is important for the appreciation of an inverse form of that statement.

According to the general procedure of complementary tri-stimulus colorimetry, several ranges (in general, three) are selected to cover the desired part (or even whole) of the absorbance curve and several wavelengths (ordinates) in each range are selected.

The absorbance values are read at each ordinate in each range and their sum is taken. The sum, R, in the r^{th} range for all ordinates up to and including the i^{th} is then given by

$$R_r = \sum_{i}^{n} A_{r,i} \tag{1}$$

where A is the absorbance. The complementary colour co-ordinates can then be calculated from

$$Q_r = \frac{R_r}{\sum_{r} R_r} \tag{2}$$

In the usual procedure, equation (2) is equivalent to the three equations:

$$u = \frac{U}{U + V + W} \tag{3a}$$

$$v = \frac{V}{U + V + W} \tag{3b}$$

$$w = \frac{W}{U + V + W} \tag{3c}$$

where for $r = 1, 2$ and 3, R_r becomes U, V and W, and Q_r becomes u, v and w, respectively. As can be seen, the complementary colour co-ordinates (u, v and w) are concentration independent. The sum $U + V + W$ is denoted as J and may be called the "optical concentration". It is related to the analytical concentration C by the relation

$$J = E \times C \times l \tag{4}$$

where E is the overall absorptivity and l is the length of the light path through the absorbing solution.

The complementary colour co-ordinates of a mixture of any number of colorants are given by the equation

$$Q_{r,m} = \frac{\sum_{i} C_i \times Q_{r,i} \times E_i}{\sum_{i} C_i \times E_i} \tag{5}$$

provided that Beer's law is obeyed by each colorant at each of the selected ordinates and that there is no interaction between the colorants.

In the case of an equilibrium of the type

$$M + Y \rightleftarrows MY$$

where, disregarding charges, M represents a metal ion, Y a complexing agent and MY the 1:1 complex of the two, the treatment takes the following form.

The following equations are given and hold for every state of the equilibrium:

$$K = \frac{[MY]}{[M][Y]} \tag{6}$$

$$C_M = [M] + [MY] \tag{7}$$

$$C_Y = [Y] + [MY] \tag{8}$$

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where K is the stability constant of the complex, and C_M and C_Y are the total (analytical) concentrations of the metal and the complex-forming reagent. Charges have been omitted because they are irrelevant to the present discussion and would only serve to confuse the presentation. It may be emphasised that it is the *apparent* (sometimes also called effective or conditional) stability constant which is involved in this equation. This can be calculated from the absolute constant by taking α and β factors into account in order to correct, respectively, for any influence due to pH and the presence of any other complexing agent. For this calculation see, for example, references 9, 10.

In general, it must be assumed that all three species exhibit colour *i.e.* absorb light. In that case, the complementary colour point of the system in any state of equilibrium is given according to (5), by

$$Q_{r,m} = \frac{[M]Q_{r,M}E_M + [Y]Q_{r,Y}E_Y + [MY]Q_{r,MY}E_{MY}}{[M]E_M + [Y]E_Y + [MY]E_{MY}} \tag{9}$$

By combining (9) with (7) and (8), so as to eliminate [Y] and [MY], the following is obtained

$$Q_{r,m} = \frac{\begin{array}{c}[M](Q_{r,M}E_M + Q_{r,Y}E_Y - Q_{r,MY}E_{MY}) \\ + C_M(Q_{r,MY}E_{MY} - Q_{r,Y}E_Y) + C_Y Q_{r,Y}E_Y\end{array}}{[M](E_M + E_Y - E_{MY}) + C_M(E_{MY} - E_Y) + C_Y E_Y} \tag{10}$$

[M] in equation (10) is expressed by

$$[M] = \frac{1}{2K}\{[K(C_M - C_Y) - 1] + \sqrt{[K(C_M - C_Y) - 1]^2 + 4KC_M}\} \tag{11}$$

which is readily obtained from a combination of equations (6)–(8).

Inspection of (10), with [M] replaced according to (11), reveals that a plot of Q_r versus C_M or C_Y yields a rather complicated curve which would be difficult to treat.

Differentiation of $Q_{r,m}$ in the combination (10)–(11) with respect to C_Y in order to locate any possible relative maxima and/or minima yields a higher order equation which cannot be interpreted. Some interesting information can, however, be obtained from a u–v, u–w or v–w plot, whichever is most suitable.

Equation (10) is actually equivalent to three equations (with r = 1, 2 and 3) and can readily be solved for [M] yielding:

$$[M] = \frac{\begin{array}{c}[C_M(Q_{r,MY}E_{MY} - Q_{r,Y}E_Y) + C_Y Q_{r,Y}E_Y] \\ - Q_{r,m}[C_M(E_{MY} - E_Y) + C_Y E_Y]\end{array}}{Q_{r,m}(E_M + E_Y - E_{MY}) - (Q_{r,M}E_M + Q_{r,Y}E_Y - Q_{r,MY}E_{MY})} \tag{12}$$

By inserting $Q_{1,m}$ ($= u_m$) and $Q_{2,m}$ ($= v_m$) for r = 1 and 2, respectively, and equating the expressions obtained in order to eliminate [M], the desired relationship between u_m and v_m is obtained:

$$\begin{array}{c}\dfrac{C_M(u_{MY}E_{MY} - u_Y E_Y) + C_Y u_Y E_Y - u_m[C_M(E_{MY} - E_Y) + C_Y E_Y]}{u_m(E_M + E_Y - E_{MY}) - (u_M E_M + u_Y E_Y - u_{MY}E_{MY})} \\ = \dfrac{C_M(v_{MY}E_{MY} - v_m E_Y) + C_Y v_Y E_Y - v_m[C_M(E_{MY} - E_Y) + C_Y E_Y]}{v_m(E_M + E_Y + E_{MY}) - (v_M E_M + v_Y E_Y - v_{MY}E_{MY})}\end{array} \tag{13}$$

Solution for v_m yields

$$v_m = \frac{\begin{array}{l} u_m\{[C_M(E_{MY} - E_Y) + C_Y E_Y](v_M E_M + v_Y E_Y - v_{MY} E_{MY}) \\ - [C_M(v_{MY} E_{MY} - v_Y E_Y) + C_Y v_Y E_Y](E_M + E_Y - E_{MY}) \\ + [C_M(v_{MY} E_{MY} - v_Y E_Y) + C_Y v_Y E_Y](u_M E_M + u_Y E_Y - u_{MY} E_{MY}) \\ - [C_M(u_{MY} E_{MY} - u_Y E_Y) + C_Y u_Y E_Y](v_M E_M + v_Y E_Y - v_{MY} E_{MY}) \end{array}}{\begin{array}{l} [C_M(E_{MY} - E_Y) + C_Y E_Y](u_M E_M + u_Y E_Y - u_{MY} E_{MY}) \\ - [C_M(u_{MY} E_{MY} - u_Y E_Y) + C_Y u_Y E_Y](E_M + E_Y - E_{MY}) \end{array}} \qquad (14)$$

Since v_m is a function of C_M and C_Y as well as of u_m, there is no simple relationship between u_m and v_m even when C_M or C_Y or their sum is held constant. Frequently, however, the complexing agent is colourless, or at least a range can be chosen in which it does not absorb. In that case, $E_Y = 0$ and equation (14) collapses to the simple straight line relationship:

$$v_m = \frac{u_m(v_M - v_{MY}) + u_M v_{MY} - u_{MY} v_M}{u_M - u_{MY}} \qquad (15)$$

Analogous expressions of equal simplicity are obtained for cases with E_M or E_{MY} = zero.

Hence, the important conclusion is obtained that *more than two colorants must be present if the u–v (or u–w or v–w) plot is not a straight line.* It should be emphasised that a colorant in this respect is a species which absorbs in any or all of the ranges selected. It is, however, of utmost importance to appreciate that the inverse of the above conclusion is *not* valid: that is, the occurrence of a straight line in a u–v plot does not necessarily indicate the presence of a simple equilibrium. It may, however, strongly support any evidence to that effect derived from other measurements.

It is also possible to study the dependence of an equilibrium upon variation of the pH or of the concentration of one of the reactants. A u–pH or a u–C plot will yield a straight line, parallel to the pH or C axis (usually plotted as the abscissa), if these factors do not affect the equilibrium. A horizontal line will also be obtained during the range where a complex is formed gradually, since the value of u is concentration independent. Thus, for example, a u–pH plot will reveal the existence and pH range of each colorimetrically unique complex in a system, and over each range in which a stable form occurs the line will be parallel to the abscissa, provided, of course, that there is no overlapping of consecutive steps. The non parallel portions of such a plot indicate the ranges of transition from one form to another.

With this information at hand, the results of several series of experiments, performed in connection with the investigation of the mixed copper aluminium tartrate complex, can be discussed.

EXPERIMENTAL

All reagents used in this investigation were of analytical grade. d-Tartaric acid was used in all experiments. The absorbance curves were obtained with a Cary 14 recording spectrophotometer. The photometric time studies were performed employing a Bausch and Lomb Spectronic 20 photometer. The time effect on pH was studied employing a Leeds and Northrup pH-meter and a Sargent recorder.

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RESULTS AND DISCUSSION

A typical absorbance curve for the copper tartrate complex in the region 350–900 mμ shows a very strong absorbance up to about 400 mμ. The curve then drops sharply, almost to zero, and rises slowly to a maximum in the nearest infrared. The location and, to some extent, the height of the latter maximum are dependent upon the pH. For this reason, the region from 600–900 mμ was utilised for further investigations. In order to obtain thorough coverage of this region the following ranges were selected: u-range, 600–690 mμ; v-range, 700–790 mμ; w-range, 800–890 mμ.

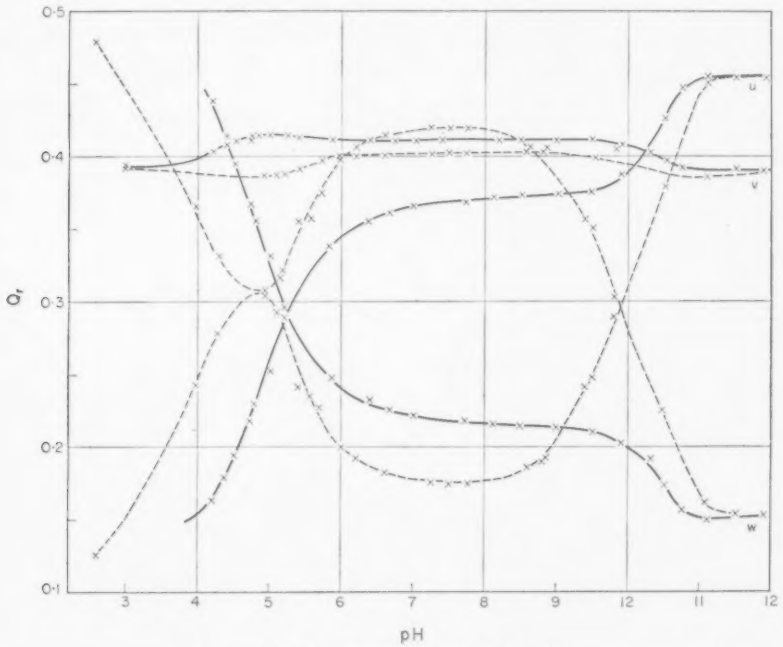

FIG. 1.—Dependence of Q_r on pH.
Solid curves: solution 0·02M in copper and 0·05M in tartrate.
Broken curves: copper and tartrate concentrations as above and 0·0385M in aluminium

Each range contained ten ordinates at 10-mμ intervals. The u, v and w values were computed in the manner previously described.[6]

The solid curves in Fig. 1 show the variation of u, v and w values with the pH of a solution 0·02 M in copper nitrate and 0·05 M in tartrate. These values were computed from absorbance curves obtained at various pH values; some of those curves are shown in Fig. 2. Below pH 4, the u–pH curves approach the horizontal. It was difficult to obtain reliable results in this region because precipitation occurred, especially at the higher tartrate concentration used in later experiments. No effort has been made to obtain complete information below pH 4 since it is not relevant to the present investigations. It is possible, to a certain degree, to reconcile this curve with some of the data reported in the literature. Fronaeus[11] reported the following stability constants of copper tartrate complexes: $\log K_1 = 3{\cdot}20$; $\log K_2 = 1{\cdot}91$; $\log K_3 = -0{\cdot}34$ and $\log K_4 = 1{\cdot}73$. The values are for d-tartaric acid, which has also been used in the experiments reported in the present paper. These data explain the contention of Sen Sarma[12]

that only a 1:1 complex exists in very dilute acid solutions. In the pH range with which the present study is concerned, hydroxo complexes clearly must be taken into consideration. Various types have been reported.

Tikhonov and Belskaya[13] reported the existence of the following species, where T stands for the tartrate ion: CuT in the range pH 2–5; $Cu(OH)T^-$ at pH 5·3–9, and $Cu(OH)_2T^{2-}$ at pH 9–13.5. This would agree with the trend of the curves in Fig. 1.

Souchay and Lefebre[14] reported the equilibrium:

$$Cu_3(OH)_6T_3^{6-} \rightleftarrows Cu(OH)_2T_2^{4-} + \text{excess } T^{2-},$$

the species on the left side being present at pH 8 when tartrate and copper are present in a molar ratio of 2:1. Ablov and Popovich[15] assumed a molar ratio for Cu:T of 4:3 in

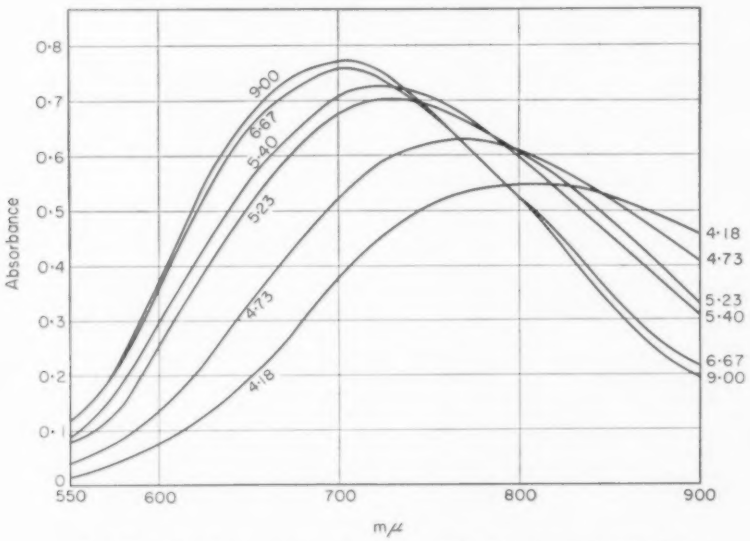

FIG. 2.—Absorbance curves of solutions 0·02*M* in copper and 0·05*M* in tartrate at various pH values

higher tartrate concentrations at about pH 7. They included no hydroxo ligands in their formulation.

Curves similar to Fig. 1 have been obtained for the system with increasing tartrate concentrations and are presented as solid curves in Figs. 3, 4 and 5. Since no additional information can be obtained from *v* and *w* curves only the *u* curves are shown.

All curves approach the horizontal at about pH 4; this may be attributed to the formation of the species CuT or at even lower pH values of $CuHT^+$. All curves approach the horizontal at pH values higher than 10, though at a slightly different level. At very high pH values (not shown because it is not pertinent to the present study), a further change in equilibrium is indicated which can be attributed to the formation of the cuprate ion.[14]

At low tartrate concentrations, the middle part of the curves in the pH range 5–10 may be related to the existence of the complex $Cu(OH)T^-$ according to Tikhonov and Belskaya.[13] At higher tartrate concentrations the co-ordination requirements of

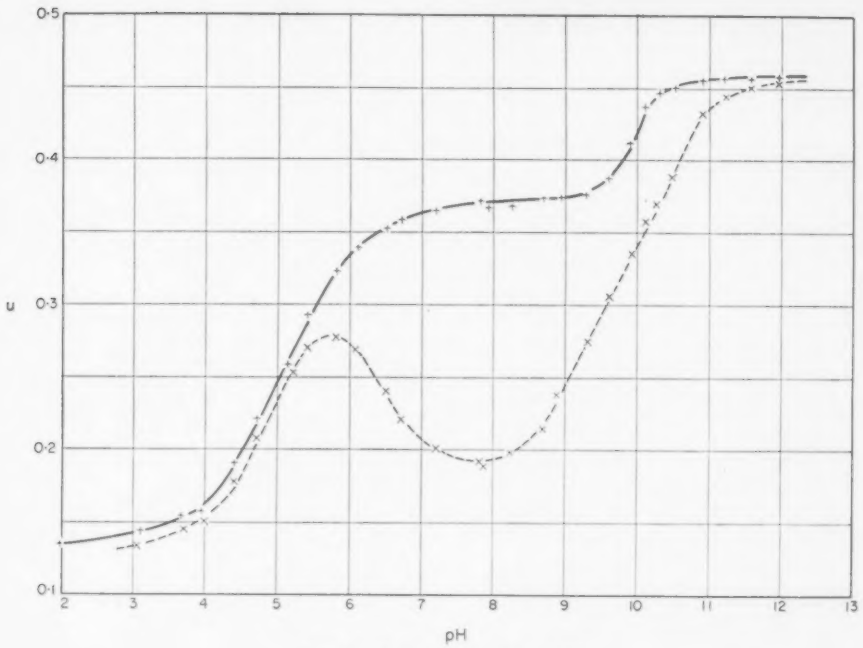

FIG. 3.—Dependence of u on pH.
Solid curve: solution 0·02M in copper and 0·1M in tartrate.
Broken curve: copper and tartrate concentrations as above and 0·0385M in aluminium.

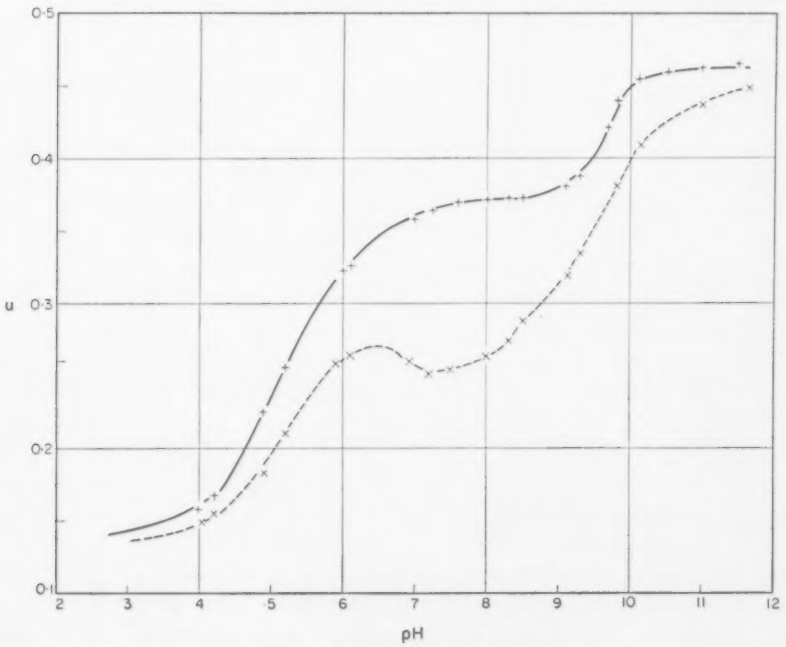

FIG. 4.—Dependence of u on pH.
Solid curve: solution 0·02M in copper and 0·2M in tartrate.
Broken curve: copper and tartrate concentrations as above and 0·0385M in aluminium.

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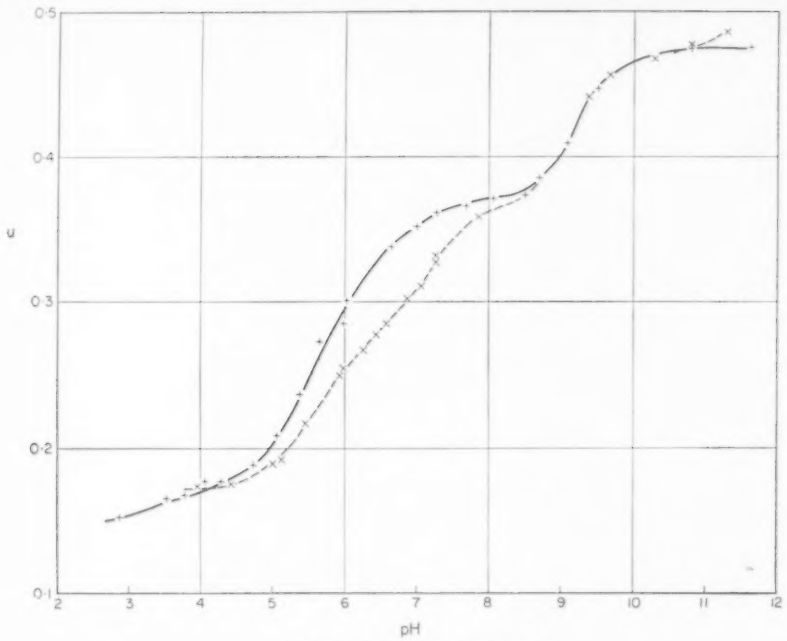

FIG. 5.—Dependence of u on pH.
Solid curve: solution 0·02M in copper and 0·5M in tartrate.
Broken curve: copper and tartrate concentration as above and 0·0385M in aluminium.

copper seem to be more and more satisfied by tartrate as opposed to the hydroxo ligand. Hence, overlapping equilibria occur and the length of the horizontal part (related to the monohydroxotartrate) shrinks, degenerating to an inflection point at a tartrate concentration of 1 M. The corresponding curves for copper tartrate from Figs. 1, 3, 4, 5 and an additional curve measured at a tartrate concentration of 1 M are collected in Fig. 6 in order to facilitate comparison.

If, indeed, the course of the complex formation is such that $Cu(OH)_2T^{2-}$ is the only species present within the pH range 9–13·5, it must be expected that all curves will return to the same level. This is not, however, the case, as is evident from Fig. 6, and it suggests the presence of a new species at high concentrations of tartrate and hydroxyl ion.

The broken curves in Figs. 1, 3, 4 and 5 represent results obtained when aluminium was present in the solution. Since neither aluminium nor its tartrate complex absorbs in the 600–900 mμ range, it is obvious that there is some reaction between aluminium and copper tartrate.

The deviations of the broken curves from the solid curves are greatest at the lowest tartrate concentration and decrease with increasing concentration of tartrate. This could be interpreted as a competition of copper and aluminium for the limited amount of tartrate and not the formation of a mixed complex. There is, however, still a pronounced deviation at higher tartrate concentrations, even when tartrate is present far in excess of the amount which would be necessary to complex both the copper and the aluminium separately. Further, at the lowest tartrate concentration either copper or aluminium should precipitate as a hydroxide in the higher pH ranges because there

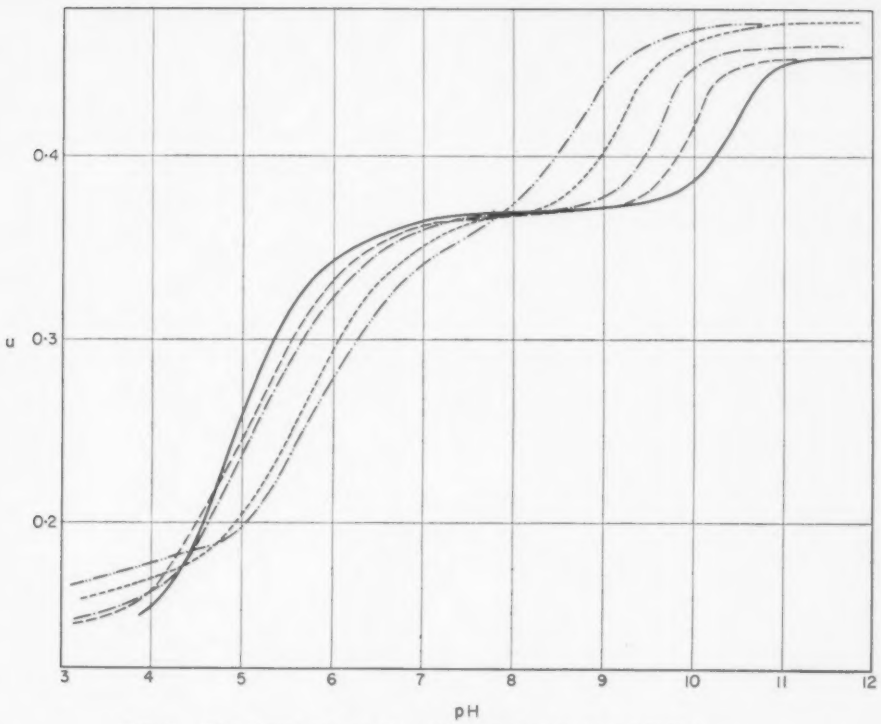

FIG. 6.—Dependence of u on pH. All curves for solutions 0·02M in copper.
Tartrate concentration ·-·-·-·- 1M
····· 0·5M
·-·-·-·- 0·2M
– – – – 0·1M
——— 0·05M

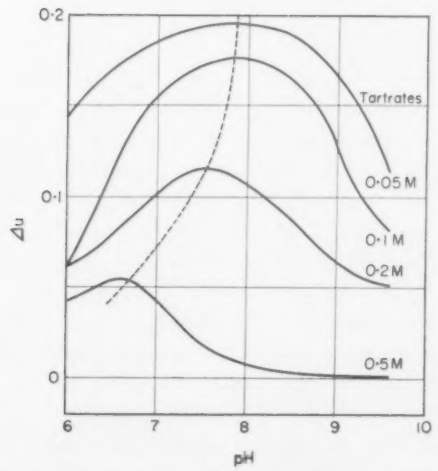

FIG. 7.—Differences in the u values of solutions with and without aluminium at different tartrate concentrations as a function of pH.

is not sufficient tartrate present to keep both metal ions complexed independently to a degree sufficient to prevent their precipitation. Hence, the only conclusion is that a complex species is formed which contains all three—copper, aluminium and tartrate. It is important to realise that this mixed complex must have a higher stability than that of the simple tartrate complex of either metal. The optical results, however, do not give any clues to the mechanism of the formation of the mixed complex.

Fig. 7 presents a plot of the differences in the *u*-values of the copper tartrate solutions, with and without aluminium present, versus pH. For low tartrate concentrations, this difference is greatest at about pH 8, which is the region in which aluminium has been found to interfere with the titration of copper with trien.[2] Several time curves were made at various pH values by mixing copper and aluminium tartrate

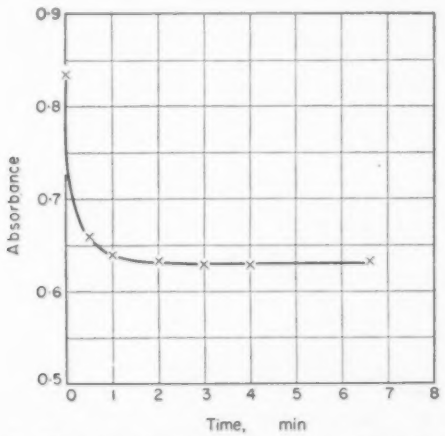

FIG. 8.—Time dependence of the formation of the mixed complex.
Equal volumes of solution A and B were mixed at time zero.
Solution A: 0·04*M* in copper; 0·1*M* in tartrate.
Solution B: 0·09*M* in aluminium; 0·1*M* in tartrate.
Initial pH = 8·00.
Absorbance measured at 700 mμ.

solutions which had been adjusted to exactly the same pH. One of these curves is shown in Fig. 8 as a representative example. Due to the rather small difference in the absorptivities of copper tartrate and the mixed complex, the effect is not very great. Similar time curves can be obtained when the formation of the mixed complex is followed polarographically. The interpretation of the polarographic curves is difficult because the pH of the solution changes during the formation of the mixed complex (see below). The time effect of the degradation of the mixed complex can be studied very effectively when the mixed complex is allowed to react with other complexing agents (see later).

Except at very high tartrate concentrations, the maximum time effect is observed in the pH range 7·5–8·0, which is exactly the range in which hydroxyl ions are part of the copper tartrate complex (see above). It is reasonable, therefore, to assume that hydroxyl ions may be released, causing a rise in pH, when the mixed comple is formed. This pH effect should, of course, also be time dependent, since it would be contingent upon the slow formation of the mixed complex. To investigate this, copper and aluminium tartrate solutions were prepared and adjusted to exactly the same pH. The

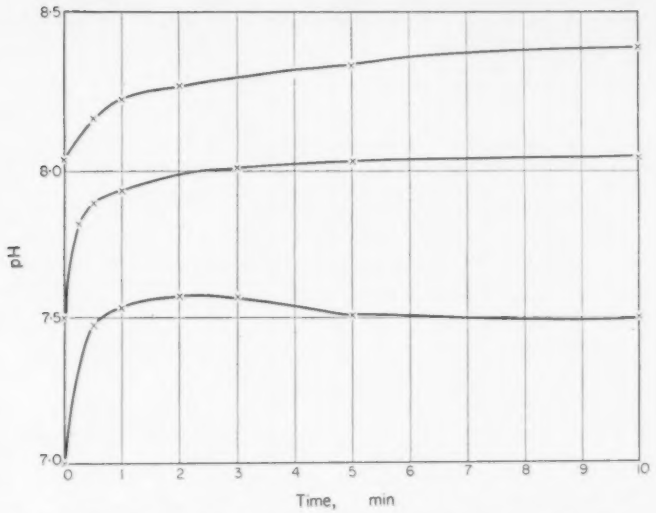

FIG. 9.—Change of pH with time after mixing solutions 0.04*M* in copper and 0·09*M* in aluminium, both solutions 0·1*M* in tartrate.

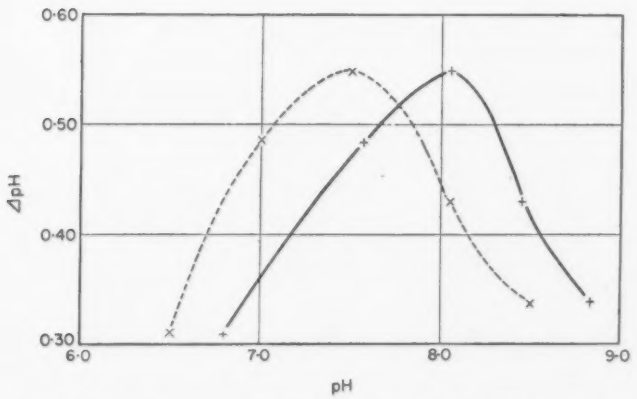

FIG. 10.—Changes in pH as a function of initial pH (dashed curve) and final pH (solid curve), obtained from data in Fig. 9.

solutions were then mixed and the pH changes with time were recorded. Some examples of the curves obtained are presented in Fig. 9. When the differences between the initial and final pH values were plotted versus the initial pH and also against the final pH, the curves in Fig. 10 were obtained.

When the mixed complex is formed with the release of hydroxyl ion, the amount of hydroxyl ion released would appear to be directly related to the copper concentration, where the aluminium concentration is kept constant. Therefore, after a constant pH value had been reached in the series of experiments described in the preceding paragraph, each of the solutions was titrated with hydrochloric acid until the initial pH value was reached again. Of course, after each addition of acid considerable time was allowed to pass in order to assure that equilibrium had definitely been reached. However, when comparing the amount of hydrochloric acid used with the copper

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concentration present, no obvious relationship could be detected. On reflection, this result is not surprising and there are several possible explanations of the discrepancy.

First, the percentage of copper present initially as hydroxo complex is not known. Furthermore, the ratio of possible mono- and dihydroxo complexes is unknown; then it must be realised that there is definite proof that the formation of the mixed complex does not go to completion. Finally, nothing is known about the aluminium tartrate, which may also be present in a hydroxo complex form and participate in the donation of hydroxyl ions. In every case considered more hydrochloric acid was needed than would correspond to 100% conversion of the copper dihydroxo complex to the mixed complex, which seems to indicate that the aluminium tartrate is indeed involved in the release of hydroxyl ions.

From the optical results secured in the present study, no conclusion can be drawn as to the mechanism involved in the formation of the mixed complex. Copper may transfer to the aluminium tartrate complex or the inverse may occur; further, it may well be that both complexes join together with the expulsion of hydroxyl ions. There are several other possibilities.

The time effect greatly depends on the form in which the aluminium is added to the copper tartrate solution. It is considerable when copper tartrate solution is mixed

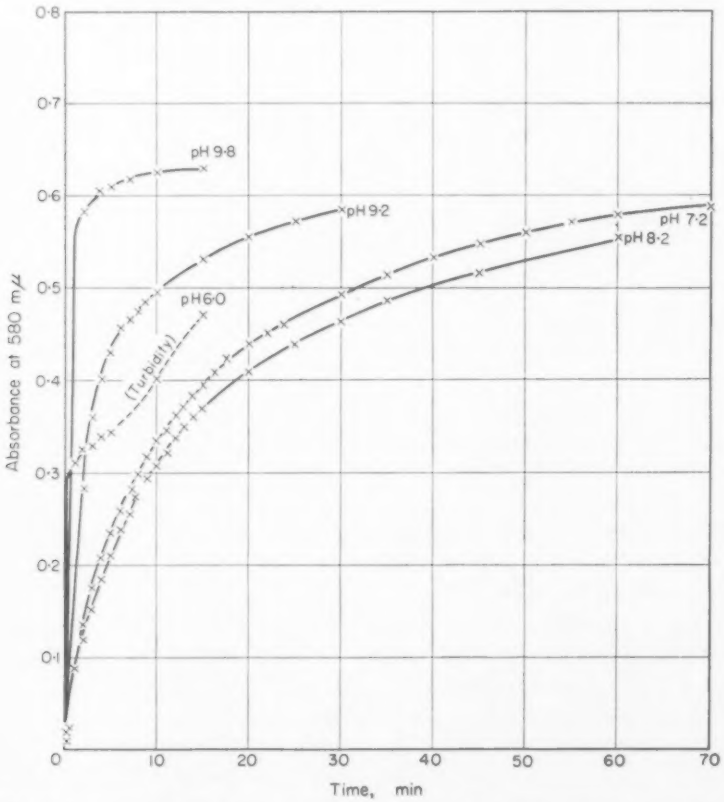

FIG. 11.—Change of absorbance (at 580 mμ) with time after adding trien to a solution 0·02*M* in copper, 0·0385*M* in aluminium and 0·1*M* in tartrate.

with an aluminium tartrate solution, both adjusted to the same pH and having equal tartrate concentration, so that the latter will not change during the mixing. However, when aluminium chloride or sulphate solution is added to the alkaline copper tartrate solution, a far greater time effect is observed. Of course, it is difficult to compare the two cases on the basis of pH effects since it is, for obvious reasons, impossible to bring the aluminium salt solution to the desired pH value. When aluminium chloride or sulphate solution is added, a neutralisation process may take first place, which leads in a first step to the formation of hydroxo compounds of aluminium, which are known

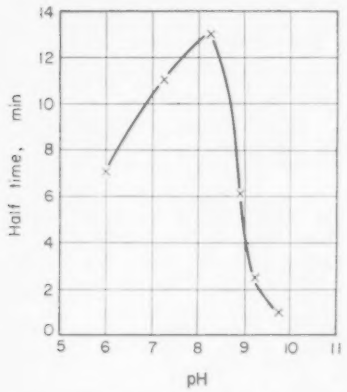

FIG. 12.—Half-time values depending on pH. Data derived from Fig. 11.

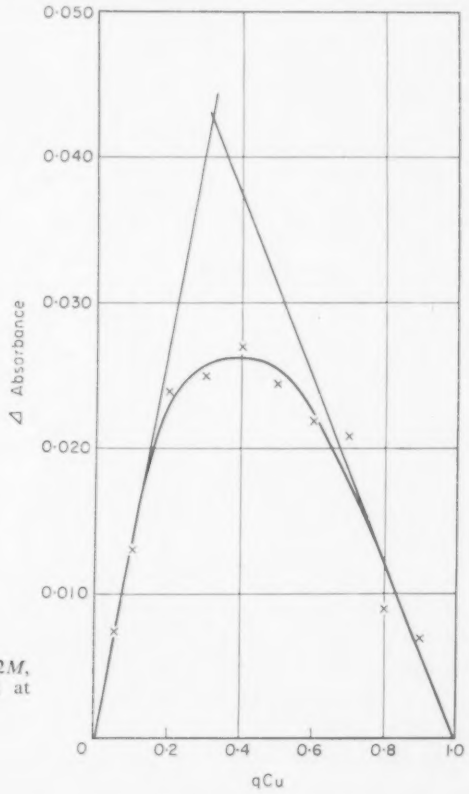

FIG. 13.—Job plot. $C_{Cu} + C_{Al} = 0{\cdot}02M$, tartrate $0{\cdot}5M$; absorbance measured at 700 mμ.

to react extremely slowly, then these species react first with tartrate or directly with copper tartrate to give eventually the mixed complex.

The mixed complex reacts slowly in any type of reaction. This has become evident in the course of the acidimetric titration of the hydroxyl ions as mentioned above. It also reacts slowly with other complexing agents which are sufficiently strong to take copper away from the mixed complex. As an example, the reaction of the mixed complex with excess trien has been studied photometrically. Some time curves obtained at various pH values are presented in Fig. 11. The half-time values (that is the time at which the absorbance reached one-half of its final maximum value) have been plotted against the initial pH and the resulting curve (Fig. 12) shows a maximum near pH 8. Of course, the exact location and also the height of that maximum are dependent on the tartrate concentration. These results are in agreement with those

obtained in the pH studies discussed above. Similar curves and identical conclusions were obtained when the replacement study was performed employing EDTA instead of trien.

In an attempt to evaluate the ratio of copper to aluminium in the mixed complex, two Job plots were made. In the first, so as to eliminate any possible effect arising from the removal of tartrate from copper tartrate by aluminium, a rather high tartrate concentration (0·5*M*) was employed, and the sum of the concentrations of aluminium and copper was kept constant at 0·02*M*. The effect, as expected, was very slight at this high tartrate concentration, and did not exceed 0·025 absorbance units. The

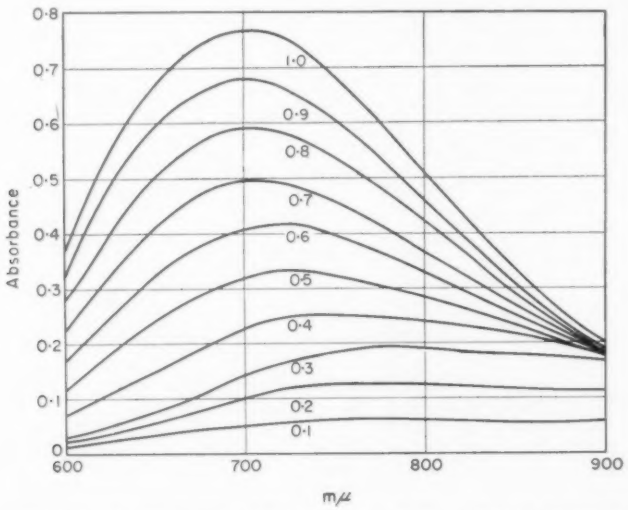

FIG. 14.—Absorbance curves for Job plot. $C_{Cu} + C_{Al} = 0{\cdot}02M$, tartrate $0{\cdot}05M$.

tangents to the straight portions of the best curve drawn through the rather badly scattered points intersect at a copper mole fraction of about 0·3. Application of the method of least squares, utilising the points $q_{Cu} = 0{\cdot}0$, 0·1 and 0·2 for the left branch and 0·6, 0·7, 0·8, 0·9 and 1·0 for the right branch, placed the intersection at $q_{Cu} = 0{\cdot}32_5$ (Fig. 13).

It is, however, very risky to base a definite conclusion on so small an effect, so a second Job plot was made at a tartrate concentration of 0·05 *M*. The absorbance curves obtained are presented in Fig. 14 and the Job curve in Fig. 15. In this case, the intersection is clearly at $q_{Cu} = 0{\cdot}33$ (the same value was obtained by the least square method), thus indicating a ratio for Cu: Al of 1: 2. In the light of this result the conclusion obtained from the Job plot at the higher tartrate concentration can be accepted.

In order to investigate further the situation at higher tartrate concentrations, the mole ratio method was applied. Increasing amounts of aluminium were added to solutions 0·02 *M* in copper and 0·5 *M* in tartrate. The pH of each solution was adjusted to about 6·6 and the solutions were allowed to stand overnight. The pH was then brought to exactly 6·60 and an acetate buffer of that pH was added. After another day the pH was checked again and re-adjusted if necessary. The pH value of 6·60 was chosen because at this pH the difference in absorbance of solutions with and without aluminium is greatest at a tartrate concentration of 0·5 *M* (see Fig. 7).

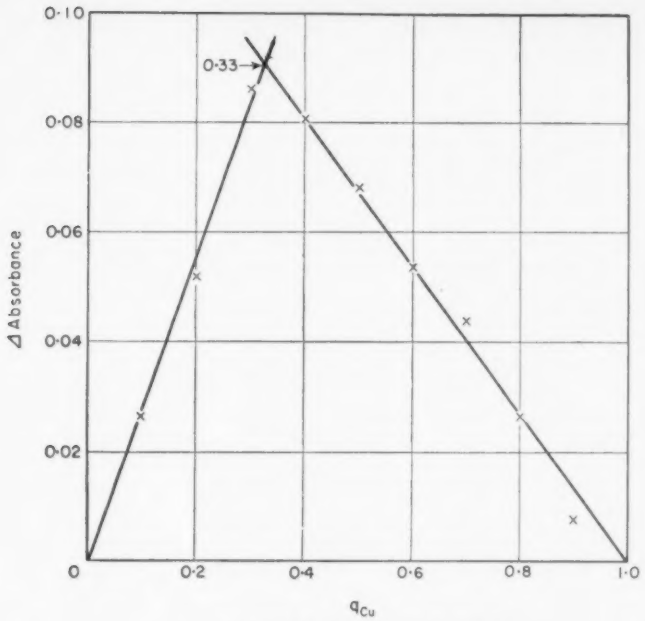

FIG. 15.—Job plot of data in FIG. 14.

Absorbance curves were obtained for all of these solutions and the absorbance at 700 mμ was plotted against the molar ratio of aluminium to copper. The plot is shown in Fig. 16. Amazingly there are three straight branches. The first intersection is at a molar ratio for Al:Cu of about 2:1 which is in agreement with the Job plot. There is,

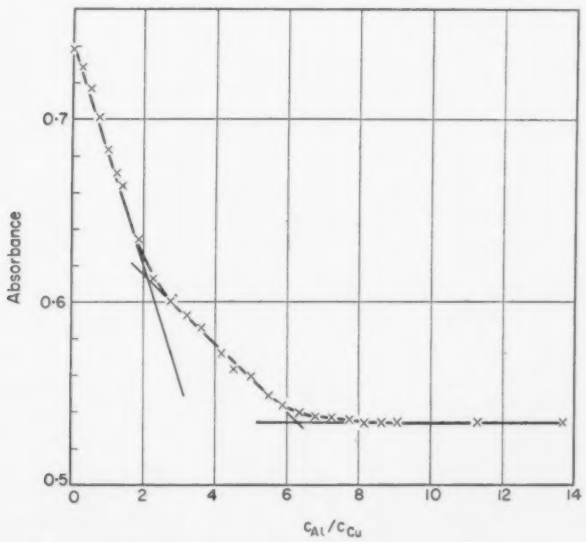

FIG. 16.—Method of constant variation. $C_{Cu} = 0{\cdot}02M$ = constant; tartrate $0{\cdot}5M$; pH 6·60; absorbance readings at 700 mμ.

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however, an indication of a second complex with the ratio in the neighbourhood of 6:1, forming at very high aluminium contents. The discrepancy between the results obtained by the two different methods cannot be explained.

Further evidence for the fact that some rather complicated reactions are involved is obtained from a u–w plot which is presented in Fig. 17. Some portions of the line are definitely curved, indicating the presence of equilibria involving more than two coloured species.

In order to demonstrate further the pH dependence of the equilibria involved, u–v plots of copper tartrate and copper aluminium tartrate solutions were made, two of

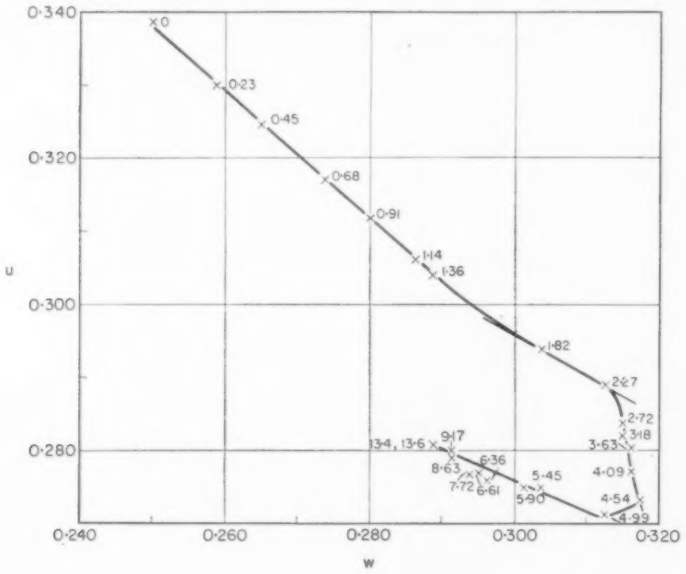

FIG. 17.—u-w Plot of the data of method of constant variation. Numbers at the curve relate to the ratio C_{Al}/C_{Cu}.

which are presented in Fig. 18. Only straight line plots were obtained from the aluminium-free solutions, each straight portion corresponding to the transition from one equilibrium to another. The regions in which only one species predominates are represented by a point or by a closely grouped collection of pH points. As shown in the theoretical section of this paper, the straight lines in these u–v plots may indicate, but do not prove, the presence of a simple equilibrium. The three branches of the line for 0·05 M copper solution (with no aluminium present) may be attributed, respectively, to the transitions:

$$\mathrm{Cu} \rightleftharpoons \mathrm{CuT} \quad \text{or possibly} \quad \mathrm{CuHT} \rightleftharpoons \mathrm{CuT} \qquad \text{(I)}$$

$$\mathrm{CuT} \rightleftharpoons \mathrm{Cu(OH)T} \qquad \text{(II)}$$

$$\mathrm{Cu(OH)T} \rightleftharpoons \mathrm{Cu(OH)_2T} \qquad \text{(III)}$$

Fig. 18 presents u–v plots for a solution also containing aluminium (broken curves). Here there are many more transitions and more complicated equilibria are involved. At the present state of development of complementary tri-stimulus colorimetry this is the only conclusion which can be drawn. It is impossible, at present, to relate the

different parts of the curve to specific equilibria. In fact, it is doubtful if optical results alone will ever suffice to that end. pH titrations of copper aluminium tartrate solution would provide additional information, but because of the very slow reaction rates, this would be tedious and has not been attempted.

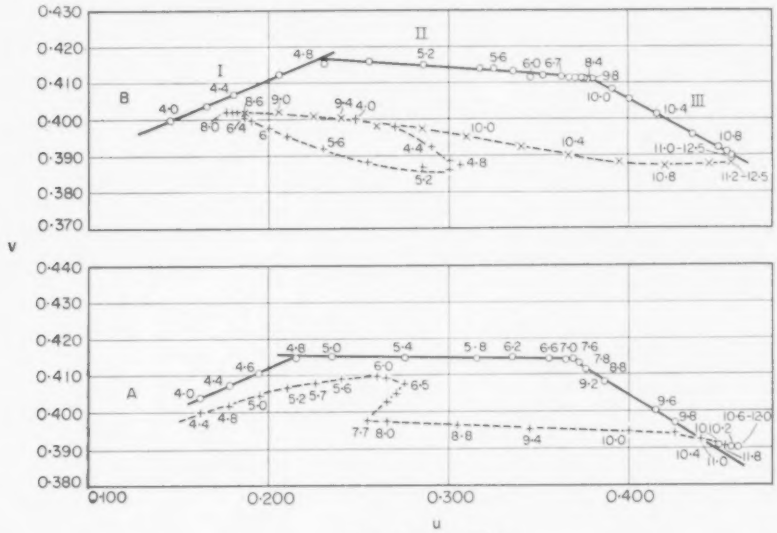

FIG. 18.—*u-w* Plots.

A: solid curve: solution 0·02*M* in copper and 0·2*M* in tartrate.
broken curve: copper and tartrate concentrations as above and 0·0385*M* in aluminium.
B: solid curve: solution 0·02*M* in copper and 0·05*M* in tartrate.
broken curve: copper and tartrate concentrations as above and 0·0385*M* in aluminium.
Numbers adjacent to the curves refer to the pH values.

CONCLUSION

When copper, aluminium and tartrate ions are present in a neutral or slightly alkaline solution a mixed complex is formed. This mixed complex may also contain some hydroxo groups. The stability of the mixed complex is greater than that of the tartrate complexes of the two metals, as can be deduced from the fact that the mixed complex forms to an appreciable amount even at tartrate concentrations which are more than sufficient to complex both metals separately. Further corroboration is obtained from the fact that no precipitation of the metal hydroxides is observed in an alkaline solution containing far too little tartrate to complex both metals separately. The formation of the mixed complex is pH dependent and reaches a maximum between pH 6 and 8, depending on the tartrate concentration. The lower the tartrate concentration, the higher the pH at which maximum formation of the mixed complex occurs. Both formation and cleavage of the mixed complex are slow processes which can be followed photometrically. At the pH range in which the mixed complex is stable, hydroxo groups are present in the copper tartrate complex and most probably also in the aluminium tartrate complex. Hydroxyl ions are released during the formation of the mixed complex and hence the formation may be followed via pH measurements. At low tartrate concentrations, the molar ration of Cu : Al in the mixed complex is 1 : 2. At high tartrate and aluminium concentrations this ratio is uncertain and results

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obtained by the method of constant variation suggests that the ratio has a different value or that at least two different complexes are present.

Acknowledgement—The work was carried out with the aid of the National Science Foundation. Mr. A. Chason and Mr. A. Shingler of The Coca Cola Company, Atlanta, Ga., arranged permission to use the Cary recording spectrophotometer of the company. Dr. A. J. Barnard, Jr., Phillipsburg, N.J., offered valuable criticism of the manuscript. All of this assistance is gratefully acknowledged.

Zusammenfassung—Die Theorie der komplementären Tristimuluskolorimetrie wurde erweitert und auf das Studium von Komplexgleichgewichten angewandt. Ein Mischkomplex, der Kupfer, Aluminium und Tartrat enthäl, wurde untersucht. Der Mischkomplex ist stabiler als die einfachen Tartratkomplexe von Kupfer und Aluminium und wird auch gebildet, wenn Tartrat in beträchtlich höherer Konzentration anwesend ist, als zur Bildung der einfachen Metallkomplexe benötigt wird. Die Bildung des Mischkomplexes erfolgt langsam und auch seine Reaktionen mit anderen Komplexbildnern sind verzögert. Die Bildung des Mischkomplexes ist mit Freiwerden von Hydroxylionen gekoppelt. Der pH-Bereich, in dem der Mischkomplex existiert, wurde ermittelt und die Zusammensetzung des Komplexes studiert.

Résumé—La théorie de la colorimétrie trichrome a été étendue et appliquée à l'étude des équilibres. Un complexe mixte contenant du cuivre, de l'aluminium et du tartrate a été étudié. Le complexe mixte est plus stable que les complexes tartriques des métaux individuels, et il se forme même dans des solutions contenant plus de tartrate qu'il n'est nécessaire pour former les complexes simples. La formation du complexe mixte est lente, de même que sa réaction avec d'autres substances formant des des complexes. La formation du complexe mixte est accompagnée de la libération d'ions hydroxyles. Le domaine de pH dans lequel existe le complexe mixte a été déterminé, et sa composition a été étudiée.

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SEPARATION AND COLORIMETRIC DETERMINATION OF TRACE QUANTITIES OF MAGNESIUM IN HIGH-PURITY BERYLLIUM OXIDE*

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Summary—A colorimetric method is described for the determination of trace quantities of magnesium in beryllium metal and its oxide. Beryllium, which is known to interfere with the colorimetric determination of magnesium by the available chromogenic reagents, is separated from the magnesium by forming the beryllium perfluorobutyrate salt at pH 3 to 4, and then extracting it with several portions of diethyl ether. By increasing the number of equilibrations with ether, as much as 1 g of beryllium can be separated from 10 μg of magnesium. The magnesium is then measured spectrophotometrically as the highly coloured complex with Magon, sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido) naphthalene-1-(2-hydroxybenzene-5-sulphonate), which exhibits a peak of maximum absorbance at 510 mμ. Over the range of 0·04 to 0·40 μg of magnesium per ml, the absorbance conforms to Beer's law. The method has been applied successfully to the determination of quantities of magnesium as low as 10 μg. The coefficient of variation for samples which contain 200 μg of magnesium is 2%.

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METHODS for the determination of trace quantities of magnesium in high-purity beryllium metal and its oxide are generally unsatisfactory. Despite the high order of sensitivity afforded by a number of reagents for magnesium, such as Eriochrome Black T,[3,8,9] Thiazole yellow,[1,2] and Magon,[4,5] suitable precision in the range of 1 to 100 ppm is lacking. This situation is probably because of incomplete separation of beryllium which is known to interfere with the above reagents for magnesium. Mills and Whetsel,[7,8] in their investigation of the extraction properties of perfluorocarboxylic acids, found that beryllium behaved uniquely in that it was extractable, in contrast to the other bivalent cations. By combining this separation technique with the highly sensitive reagent, Magon, sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido) naphthalene-1-(2-hydroxybenzene-5 sulphonate), a reliable precise method for the determination of traces of magnesium in beryllium metal and its oxide has been developed and applied successfully.

EXPERIMENTAL

Reagents

Stock solution of magnesium: Prepared by dissolving 3·4 g of $MgCl_2 \cdot 6H_2O$ in 200 ml of 1*M* hydrochloric acid in a polyethylene bottle. This solution was standardised gravimetrically by the di-ammonium phosphate method.

Borax buffer solution, 0·08M: Prepared by dissolving 3·05 g of $Na_2B_4O_7 \cdot 10H_2O$ in 100 ml of water.

Ether, anhydrous reagent grade.

Perfluorobutyric acid-sodium salt (*NaPFB*) (Minnesota Mining and Manufacturing Co.), 1*M* solution: Prepared by neutralising 13 ml of the reagent with sodium hydroxide before dilution to 100 ml with water. When stored in a polyethylene container this reagent is stable indefinitely.

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† Work carried out under contract No. W–7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Polyvinyl alcohol (Elvanol, du Pont grade 52–22), 2% solution: Prepared by dissolving 2 g in 100 ml of water. When stored in a refrigerator this reagent is stable for about 1 month.

Reagent solution (*Magon*) (LaMotte Chemical Products Co.,), 0·015%: Prepared by dissolving 30 mg of sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido)naphthalene-1-(2-hydroxybenzene-5-sulphonate) in 200 ml of ethanol. This reagent is stable for at least 1 month.

Apparatus

A Cary Model 14-M recording spectrophotometer was used to obtain the spectra reported here. Matched fused 1-cm Corex cells were used.

RESULTS AND DISCUSSION

Effect of polyvinyl alcohol

In their investigation of the determination of magnesium by the Magon method, Mann and Yoe[4] reported that for accurate measurements it was necessary to hold the pH fairly constant. This was done by making the magnesium solution, from which aliquots are taken, just acid to phenolphthalein. Observing these conditions, it was found that 30 μg of beryllium in the test aliquot caused an error of about 5% in the magnesium determination. McCann,[6] in his determination of magnesium by the Thiazole yellow method, added a dispersing agent, polyvinyl alcohol, to the solutions under investigation before adding the chromogenic reagent. When polyvinyl alcohol is added to the magnesium solutions before adjusting the pH in the Magon method, a weight ratio of beryllium to magnesium as great as 200:1 could be tolerated.

Since magnesium is usually contained in beryllium metal and its oxide as a trace quantity, rarely exceeding 200 ppm in any given determination of magnesium, the ratio of beryllium to magnesium contained in the test aliquot would most likely be greater than 200:1. Therefore the excess of beryllium which is known to interfere with the method must be removed in some manner.

Extraction of beryllium

The most logical approach in the determination of traces of impurities in highly purified materials is, when necessary, to separate the minor component from the matrix. Since no suitable method is available for completely separating magnesium from the beryllium matrix, attention was turned to methods for reducing the matrix concentration as much as possible.

Mills and Whetsel,[7] in their investigation of the uses of perfluorocarboxylic acids as separating agents, found that many multivalent and a few bivalent cations, which include beryllium, are separated from univalent and the other bivalent ions using perfluorobutyric acid as the extracting agent and ethyl ether as the second solvent. Their extraction data are based on the fact that the perfluorocarboxylic acids are increasingly more soluble in the organic solvent than in aqueous media. Further, upon evaporation of the ether extracts they found that the extracted species is a basic salt. Utilising the data of Mills and Whetsel,[7] the separation of beryllium from magnesium by extracting the beryllium into perfluorobutyric acid in ether was investigated.

Dilutions of perchloric acid solutions of beryllium were taken to determine the extraction characteristics of beryllium with perfluorobutyric acid in ether. The pH of the solutions was adjusted to the range 1·0 to 5·0. After adding 0·5 mmoles of

perfluorobutyric acid for each mg of beryllium present, the solutions were equilibrated for 2 min. As shown in Fig. 1, the extraction is dependent on the pH of the aqueous solution. At a pH of 1·0, little extraction of the beryllium occurs; at a pH of 2·0, the extraction coefficient is about 4. Precipitation occurs when the pH is adjusted to 5·0. When the pH of the aqueous solution is adjusted to 3·0 to 4·0, about 96% of the beryllium is removed by a single extraction. These results agree well with the

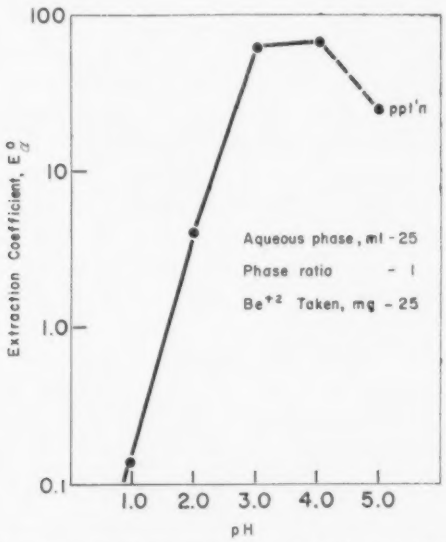

FIG. 1.—Effect of pH on the extraction of Be^{2+} with NaPFB in ether.

data of Mills and Whetsel,[8] who stated that extractions using the perfluorocarboxylic acids proceed best at a pH slightly less than that at which the cation would form an insoluble hydroxide. On the basis of these results, when the magnesium is contained in beryllium oxide in the range of 100 to 200 ppm, sufficient quantities of beryllium are removed to permit an accurate measurement of the magnesium by a single extraction. When the magnesium is of the order of 0 to 100 ppm, however, additional extractions with ether are required. Since the maximum quantity of beryllium that can be tolerated in the test aliquot of magnesium has been determined, and since about 96% of the beryllium is removed by each equilibration, the number of ethereal extractions necessary to remove the prescribed amount of beryllium can be calculated. No additional perfluorobutyric acid, however, need be added.

Other elements listed by Mann and Yoe[4] as interferences with the method include aluminium, molybdenum, chromium, iron, uranium, thorium, rare earths, and nickel. The normal separation of beryllium from magnesium by extracting the beryllium into perfluorobutyric acid in ether also removes these multivalent cations. The only ion not removed by this extraction is nickel. When present in a concentration level two times that of magnesium, nickel produces a 5% error; at a 5:1 level the error is about 30%. Fortunately, nickel rarely exceeds 100 ppm in these beryllium materials. Nickel does not, therefore, present too difficult a problem in this particular application.

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Effect of acid media

Beryllium is extracted equally well from nitric, hydrochloric, or perchloric acid solutions by perfluorobutyric acid in ether; little or no extraction occurs when the beryllium is contained in hydrofluoric or sulphuric acid solutions. This unique property can be made use of in reclaiming the perfluorobutyric acid. The beryllium is back-extracted from the combined ether extracts into 4*M* sulphuric acid, the ether is evaporated, and the reclaimed acid is then ready for future use.

Effect of perfluorobutyric acid

Tests were conducted to determine the effect of perfluorobutyric acid on the colorimetric determination of magnesium. Aliquots of the stock solution of magnesium were diluted with perfluorobutyric acid ranging from 1 to 10 mmoles of the acid. This represents the greatest concentration of perfluorobutyric acid to be encountered in the analysis. From these test solutions aliquots were taken for the magnesium determination by the colorimetric Magon method.

As shown in Table I, perfluorobutyric acid does not affect the absorbance of the magnesium-Magon complex over the range of acid concentration tested.

Table I.—Effect of perfluorobutyric acid on the colorimetric determination of magnesium

Magnesium, 10 μg	
Perfluorobutyric acid, *mmole*	Absorbance
—	0·512
2·5	·498
5·0	·508
7·5	·528
10·0	·520

The spectrum of the solution of the magnesium complex containing perfluorobutyric acid is identical with the standard magnesium complex. There are two absorption peaks, the maximum occurring at 510 mμ. At this wavelength an absorbance index of 26,500 was reported by Mann and Yoe. The value found in this laboratory, 26,000 is in quite good agreement. This relationship is shown in Fig. 2.

Application to magnesium solutions which contain large amounts of beryllium

Tests were conducted to determine whether, by observing the aforementioned conditions, beryllium could be separated from magnesium in sufficient quantities to permit an accurate measurement of the magnesium. Beryllium was added to dilutions of the stock solution of magnesium. Following a separation of the beryllium by extracting the perfluorobutyrate into ether, the magnesium in the aqueous layer was measured colorimetrically. When the absorbance at 510 mμ is corrected for unused Magon reagent, the adherence to Beer's law is excellent; absorbance is a linear function of concentration. This relationship, which extends to solutions containing 0·4 μg of magnesium per ml (absorbance 0·5), is shown in Fig. 3.

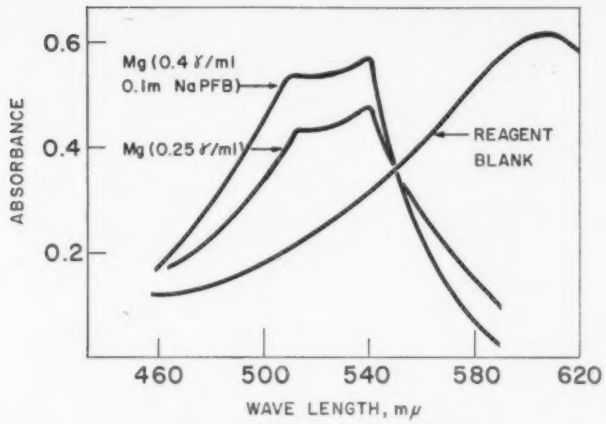

FIG. 2.—Effect of perfluorobutyric acid.
Cary recording spectrophotometer, Model 14M:
1-cm Corex cells.
Reference solution water.
Speed 10 Å/sec.

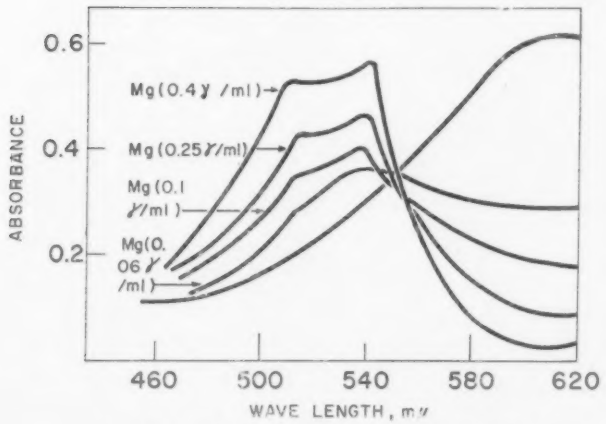

FIG. 3.—Effect of absorbance vs. concentration.
Cary recording spectrophotometer, Model 14M:
1-cm Corex cells.
Reference solution water.
Speed 10 Å/sec.

Precision of the method

The precision of the method was determined at three concentration levels of magnesium, approximately 10, 50, and 100 ppm of magnesium. In all tests the beryllium was removed by extracting it into perfluorobutyric acid in ether. The overall coefficient of variation is 2·5%. There is no indication of a bias on the basis of these results.

Application of the method

Samples of beryllium metal and its oxide which contained determined amounts of magnesium were obtained, to assess the validity of the method. Typical results for

Table II.—Precision and accuracy of the method

Magnesium, *ppm*	10	50	100
Number of determinations, N	4	4	4
Average magnesium found, $\bar{x}$	12	49	104
Coefficient of variation, %	3·6	2·1	1·9

magnesium, as analysed by the spectrophotometric method, are illustrated in Table III. The results are in excellent agreement over a wide range of magnesium concentrations. The average difference is about 2%

Table III.—Typical results for the spectrophotometric determination of magnesium in beryllium metal and its oxide

Magnesium, *ppm*		
Average value A	Found B	Difference A − B
15	17	−2
35	33	+2
40	45	−5
53	56	−3
185*	170	+15
450*	445	+5
700*	680	+20
1140	1100	+40
1500	1550	−50
4700	4730	−30

* Beryllium metal

Average	17
Coefficient of variation, %	4·5
Overall agreement, %	2

Recommended procedure

Weigh a 1- to 2-g sample of beryllium oxide to the nearest 10 mg and transfer to a platinum dish. Add 15 ml of concentrated hydrofluoric acid and 15 ml of concentrated perchloric acid. Heat to strong fumes of perchloric acid, and dilute to 200 ml with water.

Transfer an aliquot which contains 10 to 200 μg of magnesium to a 100-ml beaker, and add 1 ml of 1*M* NaPFB for each 2 mg of beryllium present. Adjust the pH of the test solution to 3–4 by the dropwise addition of a 20% sodium hydroxide solution. Transfer the solution to a 60-ml separatory funnel which contains 25 ml of ether, and equilibrate for 2 min. Drain the aqueous layer into a 50-ml beaker and place on a steam bath to drive off the soluble ether. Cool, and transfer the solution to a 25-ml volumetric flask which contains 4 ml of the polyvinyl alcohol. Add 1:4 ammonium hydroxide dropwise until the solution is just basic to phenolphthalein, and dilute to volume with water. To a 25-ml volumetric flask which contains exactly 5 ml of the Magon reagent, add an aliquot, less than 5 ml and containing 0·5 to 10 μg of magnesium. Add 0·5 ml of the buffer solution, mix and dilute to volume with ethyl alcohol. After 30 min, measure the absorbance of the samples and a blank versus water at 510 and 615 mμ. Since the absorbance at 510 mμ is the sum of the absorbances of the complex and the unreacted reagent, and since a proportional relationship exists between the absorbances at 510 and 615 mμ, the absorbance due to the magnesium is found by calculating and deducting the absorbance of the unreacted reagent.[4]

Zusammenfassung—Eine kolorimetrische Methode zur Bestimmung von Magnesium in Beryllium und dessen Oxyd wird beschrieben. Beryllium, welches bekannterweise in der photometrischen Bestimmung des Magnesiums mit üblichen Farbreagenzien stört, wird selektiv vom Magnesium abgetrennt. Dies geschieht durch Überführen des Berylliums in das Perfluorobutyratsalz bei pH 3–4 und Extraktion desselben durch wiederholtes Ausschütteln mit Äther. Durch Anwenden einer genügenden Anzahl von Extraktionsoperationen ist es möglich bis zu einem Gramm Beryllium von nur 10 μg Magnesium zu trennen. Das Magnesium wird anschliessend spectrophotometrisch bestimmt. Farbreagens ist das Natrium 1-azo-2-oxy-3-(2,4-dimethylcarboxanilido) naphthalin-1-(2-oxybenzol-5-sulphonat). Der Magnesium komplex hat ein Absortpionsmaximum bei 510 mμ. Über einen Bereich 0.04–040 μg Mg/ml wird Beer's Gesetz erfüllt. Die Methode wurde erfolgreich auf die Bestimmung von nur 10 μg Magnesium angewendet. Der Variationskoeffizient für Proben mit 200 μg Magnesium ist 2%.

Résumé—Les auteurs décrivent uné méthode colorimétrique de dosage de traces de magnésium dans le béryllium et son oxyde. Le béryllium est connu pour gêner le dosage colorimétrique par les réactifs chromogènes convenables; il est séparé sélectivement du magnésium par formation du perfluorobutyrate de béryllium à pH 3–4, puis par extraction de ce dernier par différentes portions d'éther. En augmentant le nombre d'équilibrages avec l'éther, on peut séparer 1 g de béryllium de 10 μg de magnésium. Le magnésium est ensuite dosé par spectrophotométrie sous forme d'un complexe fortement coloré avec le "magon", 1-azo-2-hydroxy-3-(2,4-diméthylcarboxanilide) naphtalène-1-(2-hydroxybenzène-5-sulfonate) de sodium; ce complexe présente un pic d'absorption maximum à 510 mμ. Dans le domaine 0,04—0,40 μg de magnésium par ml., l'absorption obéit à la loi de Beer. La méthode a été appliquée avec succès au dosage de quantités de magnésium aussi faibles que 10 μg. Le coefficient de variation pour des échantillons de 200 μg de magnésium est de 2%.

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TITRIMETRIC DETERMINATION OF VANADIUM^{III} WITH SODIUM METAVANADATE USING REDOX INDICATORS

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Summary—Conditions have been developed for the accurate titrimetric determination of vanadium^{III} with sodium metavanadate, using diphenylbenzidine, barium diphenylamine sulphonate or *N*-phenylanthranilic acid as an internal indicator. A study of the indicator-oxidant and the oxidised indicator-reductant reactions shows that a satisfactory titration of vanadium^{III} is possible at 45°–50°, in 1–3*N* hydrochloric acid containing phosphoric acid. The indicator reactions are rapid under the conditions described. The titrations are carried out in an inert atmosphere.

THE titrimetric determination of vanadium^{III} using redox indicators does not seem to have received much attention. Ramsay, Sugimoto and Vorkin[1] determined vanadium^{III} by treating a vanadium^{III} solution with an excess of standard potassium iodate solution and determining the unreacted iodate through reaction with potassium iodide. Furman and Garner[2] employed a similiar procedure. Syrokomskii and Zhukov[3] employed vanadium^{III} as a reducing titrant for the determination of potassium permanganate, potassium dichromate and vanadium^{V} using *N*-phenylanthranilic acid as indicator.

Murai[4] reported that vanadium^{III} can be determined in a mixture with vanadium^{IV} by titration with potassium permanganate, using diphenylamine as indicator. With the details available,* the present authors were unable to obtain satisfactory titrations because of the persistence of the colour of the oxidation product of diphenylamine, even after the addition of the first few drops of 0·05*N* potassium permanganate to a vanadium^{III} solution containing diphenylamine. This difficulty is doubtless due to the sluggishness of the reaction between the oxidised indicator and vanadium^{III}. This paper describes investigations on the titration of vanadium^{III} with sodium metavanadate using diphenylbenzidine, barium diphenylamine sulphonate or *N*-phenylanthranilic acid as internal indicators. Potentiometric results which will be presented elsewhere show that the reaction between vanadium^{III} and vanadium^{V} is very rapid at room temperature. Scherbina[5] gave the potential of the vanadium^{III}/vanadium^{IV} couple as +0·4 V at 18° in 1*N* solutions. Jones and Colvin[6] made measurements on cells of the type

$$Pt/VOSO_4.H_2SO_4.V_2(SO_4)_3.H_2SO_4/Hg_2SO_4.Hg$$

and calculated the standard potential of the couple to be +0·33 V at 25°. Syrokomskii and Avilov[7] gave the potential in dilute sulphuric acid as +0·359 V. The vanadium^{V}–vanadium^{IV} couple has a formal potential of 1·002 V in 0·5*M* sulphuric acid at 28°, according to our measurements. Hence it should be possible to titrate a vanadium^{III} solution with a vanadium^{V} solution using diphenylbenzidine or barium diphenylamine sulphonate as internal indicator, because they have transition potentials lying between

* *Chemical Abstracts*

those of the two systems concerned. If these expectations are to be realised in practice, it is necessary that the reaction between the indicator and vanadium^{V} and the reaction between vanadium^{III} and the oxidised indicator must both be very rapid. The observations reported in Table I show that the speed of the reaction between the indicator and sodium vanadate is slow and slightly accelerated by phosphoric acid, but not sufficiently so to make it useful in a titration. It is also not induced by the vanadium^{III}–vanadium^{V} reaction. The oxidation of diphenylbenzidine or diphenylamine sulphonic acid by vanadium^{V} in the presence of phosphoric acid becomes very rapid only at 45–50°. The results in Table II show that the reaction between the oxidised indicator and vanadium^{III} in hydrochloric acid medium is slow at room temperature, but that the addition of phosphoric acid accelerates the reaction. Even with the addition of phosphoric acid, the oxidised indicator is not reduced quickly enough by vanadium^{III} at room temperature, but is sufficiently rapid at 45–50°. Hence both reactions, the oxidation of the indicator by a trace of vanadium^{V}, and the reduction of the oxidised indicator by a trace of vanadium^{III}, require a temperature of 45–50° and acceleration by phosphoric acid to become rapid enough for a successful titration.

EXPERIMENTAL

Reagents

Vanadium^{III} solution: An approximately 0·05*M* solution of vanadium^{III} was prepared according to the procedure recommended by Lingane and Meites Jr.[8] by reduction of vanadium^{V} in an HCl–H_2SO_4 mixture in a silver reductor. The reduction was carried out in an atmosphere of nitrogen because vanadium^{III} solutions are readily oxidised by atmospheric oxygen. The concentration of vanadium^{V} was kept about 0·1*M*, that of sulphuric acid 4·5*M* and that of hydrochloric acid 7·5*M*. The solution was passed through the reductor at the rate of 30 ml per min. The reduced solution was collected in a flask containing air-free water in an atmosphere of nitrogen. The reductor was washed with air-free water and the washings were collected in the same flask. The solution was then diluted with air-free water to give nearly 0·05*M* vanadium^{III} solution and this was stored in an atmosphere of nitrogen. The solution was standardised from time to time with a standard solution of potassium iodate, according to the method of Ramsay, Sugimoto and Vorkin.[1]

Sodium metavanadate solution: A 0·05*N* sodium metavanadate solution was prepared by dissolving 5·35 g of a sample of ammonium metavanadate (Analytical Reagent grade) in water and boiling with a slight excess of sodium carbonate until free from ammonia. After cooling, the solution was made up to 1 litre. It was standardised against a standard solution of ferrous ammonium sulphate which was previously standardised against a standard solution of potassium dichromate.

Indicator solutions: A 0·1% solution of diphenylbenzidine in concentrated sulphuric acid or a 0·1% solution of barium diphenylamine sulphonate in water or a 0·1% solution of *N*-phenylanthranilic acid in a 5% sodium carbonate solution were used. Other chemicals employed in this study were of Reagent grade.

Reaction between indicator and vanadium^{V}

To 50 ml of 1·0*N* hydrochloric acid solution in a beaker, 0·05 ml of diphenylbenzidine or barium diphenylamine sulphonate was added. To this mixture was then added 0·02 ml of 0·05*M* vanadium^{V} solution. The time taken for the appearance of the colour of oxidised indicator in the absence and presence of phosphoric acid and at different temperatures was noted. The results are presented in Table I.

From Table I it is evident (1) that the oxidation of the indicator by a trace of vanadium^{V} is very slow in 1*N* hydrochloric acid at room temperature, (2) that it is accelerated by phosphoric acid, (3) that it is accelerated by a rise in temperature, and (4) that a temperature of 45–50° and the presence of phosphoric acid are necessary to make the reaction speedy enough for a successful titration.

TABLE I.—INFLUENCE OF PHOSPHORIC ACID AND TEMPERATURE ON THE SPEED OF REACTION BETWEEN THE INDICATOR AND SODIUM METAVANADATE IN 1*N* HYDROCHLORIC ACID MEDIUM

Volume of phosphoric acid, *ml*	Temperature, °*C*	Diphenylbenzidine	Barium diphenylamine sulphonate
nil	25	Blue-violet colour after 120 sec	Pale purple colour after 120 sec
nil	45	Pale blue-violet colour after 30 sec	Pale purple colour after 60 sec
5	25	Blue-violet colour in 15 sec	Pale purple colour in 25 sec
5	45	Blue-violet colour in 2 to 3 sec	Pale purple colour in 3 to 4 sec

Reaction between the oxidised indicator and vanadium^{III}

To 50 ml of 1*N* hydrochloric acid solution, 0·05 ml of 0·1 % diphenylbenzidine or of 0·1 % barium diphenylamine sulphonate was added. The indicator was oxidised by the addition of 0·02 ml of 0·05*M* sodium vanadate solution. To this mixture, kept in an inert atmosphere, was added 0·02 ml of 0·05*M* vanadium^{III} solution, and the time taken for the discharge of the colour of the oxidised indicator was noted. The results are presented in Table II.

TABLE II.—INFLUENCE OF PHOSPHORIC ACID AND TEMPERATURE ON THE SPEED OF THE REACTION BETWEEN THE OXIDISED INDICATOR AND VANADIUM^{III}

Volume of syrupy phosphoric acid, *ml*	Temperature, °*C*	Diphenylbenzidine	Barium diphenylamine sulphonate
nil	25	Colour does not disappear even in 120 sec	Colour does not disappear even in 120 sec
nil	45	Colour disappears in 40 sec	Colour disappears in 60 sec
5	25	Colour disappears in 15 sec	Colour disappears in 10 sec
5	45	Colour disappears in 1 to 2 sec	Colour disappears in 2 to 3 sec

Observations similiar to those in Table II were made in experiments conducted in 2*N* and 3*N* hydrochloric acid. These show that while phosphoric acid accelerates the reaction between the oxidised indicator and vanadium^{III}, the acceleration is not sufficient for a rapid discharge of the colour of the oxidised indicator, which is a necessary condition for a satisfactory titration. The observations in Table II also show that a rapid discharge of the colour of the oxidised indicator is produced in the presence of phosphoric acid when the temperature is raised to 45–50°. Consequently, it should be possible to carry out a visual titration of vanadium^{III} at 45–50° in 1*N* to 3*N* hydrochloric acid in an inert atmosphere (CO_2 or N_2) using diphenylbenzidine or barium diphenylamine sulphonate as internal indicator, in the presence of 5 ml of syrupy phosphoric acid per 50 ml of the titration mixture.

Recommended procedure

The titrations of vanadium^{III} with sodium metavanadate are carried out in a 200-ml tall (titration) flask fitted with a rubber stopper having 5 holes, to accommodate the inlet and outlet tubes for

nitrogen, a thermometer, and two burettes, (one burette containing sodium metavanadate solution of known strength and another burette connected to the vanadium^{III} reservoir). Simultaneous stirring and heating of the titration mixture are carried out using a B.T.L. magnetic stirrer and hot plate.

About 30 ml of 1*N* hydrochloric acid are taken in the titration flask, 2 drops of the indicator solution are added and the beaker is stoppered with all the connections duly made. Nitrogen is passed through the mixture, heated to 45–50° and stirred, for about 10 min. About 5 to 15 ml of vanadium^{III} solution are now run into the titration flask, and the mixture is titrated with the standard sodium vanadate solution at the usual speed, until the colour of the oxidised indicator persists. Typical results are presented in Table III.

TABLE III

Indicator	Vanadium^{III} taken, *m moles*	Vanadium^{III} found, *m moles*
Diphenylbenzidine	0·3026	0·3031
	0·3249	0·3254
	0·4586	0·4582
	0·6538	0·6539
	0·7368	0·7371
	0·8643	0·8641
Barium diphenylamine sulphonate	0·3265	0·3268
	0·4532	0·4536
	0·7262	0·7265
	0·8642	0·8639
	0·9486	0·9481

The use of *N*-phenylanthranilic acid has also been investigated in this titration. Even with this indicator, the addition of syrupy phosphoric acid and the use of an elevated temperature have been found necessary to accelerate the reaction between the oxidised indicator and vanadium^{III}. The acidity of the titration mixture should be kept at 4*N* with respect to hydrochloric acid. Although good results have been obtained in these titrations, it has been observed that the colour of the oxidised indicator fades away slowly after the end-point is reached, in contrast to the titration of iron^{II} with sodium vanadate at room temperature. Titrations at room temperature are possible, if carried out dropwise towards the end, and waiting for 30 sec after the addition of each drop.

Zusammenfassung—Bedingungen wurden gefunden zur genauen Bestimmung von Vanadin(III) durch Titration mit Natriumvanadat und Diphenylbenzidin, Bariumdiphenylaminsulfonat oder N-Phenylanthranilsäure als Indicator. Eine Studie der Indicatorreaktionen führte zum Schluss, dass die Titration am besten bei 45–50°C in 1–3 n Salzsäure und 5 ml sirupöser Phosphorsäure per 50 ml Titrationslösung erfolgt. Der Indicatorumschlag unter diesen Bedingungen ist rasch. Die Titration muss in inerter Atmosphäre durchgeführt werden.

Résumé—Les auteurs ont mis au point les conditions du dosage titrimétrique précis du vanadium (III) par le métavanadate de sodium, utilisant comme indicateur interne la diphénylbenzidine, le diphénylamine sulfonate de baryum ou l'acide N-phénylanthranilique. D'après une étude des réactions de l'indicateur, c'est-à-dire des réactions indicateur-oxydant et indicateur oxydé-réducteur, les auteurs ont conclu qu'un titrage satisfaisant du vanadium (III) est possible à 45–50° dans l'acide chlorhydrique 1–3 N, en utilisant 5 ml d'acide phosphorique sirupeux pour chaque portion de 50 ml du mélange à titrer. Les réactions de l'indicateur ne sont rapides que dans ces conditions. Les titrages sont effectués sous atmosphère inerte.

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SALTING-OUT CHROMATOGRAPHY—VII

ANALYSIS OF MIXTURES OF DIALKYLPHOSPHORIC ACIDS, ALKANEPHOSPHONIC ACIDS, AND ORTHOPHOSPHORIC ACID

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Summary—Attempted separations of several phosphorus acids by gas-partition and anion-exchange chromatography were unsuccessful. This paper describes a quantitative method of separation by salting-out chromatography on special Dowex 50-X4 resins of low capacity.

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ONE of the research problems of this laboratory is the development of a method of analysis of mixtures of the phosphorus-containing decomposition products of the various insecticides and similar substances. These include the alkanephosphonic acids, their monoalkyl esters, orthophosphoric acid and its dialkyl esters. The alkyl groups found in these compounds include methyl, ethyl, isopropyl and n-butyl. The symbols Pr and Bu are hereinafter used to designate the last two. This paper is concerned with a part of the whole problem, *viz.*, the separation of a mixture composed of the alkanephosphonic acids, the dialkyl esters of phosphoric acid, and orthophosphoric acid.

The phosphorus acids studied in this investigation are not sufficiently volatile to be separated by gas chromatography. A mixture consisting of the ethyl ester of methanephosphonic acid and the methyl ester of ethanephosphonic acid dissolved in ether was subjected to gas-partition chromatography at 270° and 350°. At the lower temperature, the elution graph indicated complete non-volatility. At the higher temperature, decomposition of the acids was observed. Attempted separations of the phosphorus acids by anion-exchange chromatography were unsuccessful because of the small differences in the exchange constants of their conjugate bases and in the ionisation constants of the acids themselves.[1–3]

Results obtained during the investigation of anion-exchange chromatography indicated that van der Waals forces leading to sorption of the phosphorus acids by the anion-exchange resin were of greater importance in determining the distribution coefficient than simple exchange processes. This led to the belief that a cation-exchange resin would be more suitable than an anion-exchanger for the separation of the phosphorus compounds. In the first place, the theoretical treatment with the cation-exchangers is simpler because only van der Waals forces are operating, whereas both van der Waals sorption and ion-exchange occur with the anion-exchangers. In the second place, a change in the hydrogen-ion concentration of the eluent should be more effective in changing the distribution coefficients with a cation-exchanger than with an anion-exchanger because, with the latter, an increase in the acidity of the

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eluent increases the van der Waals sorption but decreases the ion-exchange sorption. Thus, better separations may be expected with a cation-exchanger.

SALTING-OUT CHROMATOGRAPHY

The theory and applications of salting-out chromatography have been discussed in recent publications.[4–9] In this paper the basic equation of the plate theory[10]

$$U^* = CV + V \tag{1}$$

is used to calculate C values. The symbol U^* represents the volume of eluate collected from the addition of the sample to the peak of the elution graph; V is the interstitial volume of the column; and C is the distribution ratio, defined as the quantity of sample constituent in the resin of any plate divided by the quantity of the same constituent in the interstitial solution of the same plate at equilibrium. Sargent and Rieman[4] have shown that the relationship

$$\log C = \log C_0 + kM \tag{2}$$

is applicable to salting-out chromatography. Here C_0 is the distribution ratio with water as eluent; C is the distribution ratio with an aqueous salt solution of molarity M; and k is the salting-out constant. Investigation of low-capacity Dowex resins has revealed their superiority in achieving separations by salting-out chromatography.[8] Therefore, Dowex resins of low capacity were used throughout this study.

CHOICE OF ELUENT

The following compounds were investigated as possible salting-out agents: NH_4NO_3, $(NH_4)_2SO_4$, $NaNO_3$, $MgCl_2$, NaCl and LiCl. Ammonium nitrate and ammonium sulphate were rejected because of their comparatively small salting-out power. Sodium nitrate was not used because it crystallised from concentrated solutions at the tip of the stopcock attached to the ion-exchange column. Lithium chloride was chosen in preference to magnesium chloride and sodium chloride because its solutions gave a greater number of theoretical plates for the same length of column. Investigation of the effect of the hydrogen-ion concentration on the ratio of the C values for EtPO(OH)OEt and MePO(OH)OPr indicated that this ratio did not increase greatly with an increase in hydrogen-ion concentration above 1M.[1] In view of these considerations, a solution 4·0M in LiCl and 1·0M in HCl was chosen as the best possible eluent for the separation of the acids of lower molecular weight.

EXPERIMENTAL WORK

Materials

Most of the phosphorus compounds were supplied by the Army Chemical Center. The phosphonic acids $EtPO(OH)_2$ and $PrPO(OH)_2$ were prepared by hydrolysing the respective esters EtPO(OH)OPr and PrPO(OH)OEt in boiling 6M hydrochloric acid.[11] The orthophosphoric acid used was of assayed reagent-grade.

Resins of low capacity were used throughout this investigation. These resins were in every way identical to Dowex 50-X4, except that their capacities were lower than the usual value of 5·2 meq per g. Each low-capacity resin investigated consisted of spheres that passed through a 325-mesh screen and were cross-linked with 4% nominal divinylbenzene.

All eluents were prepared by dissolving assayed reagent-grade chemicals in distilled water.

Determination of the interstitial volume

The interstitial volumes of the resin columns were determined under the conditions used in this investigation, *viz.*, with eluents of 0, 2, 4, 6 and 8M LiCl, each also 1M with HCl. These values are

necessary in order to calculate C, the distribution ratios of the several phosphonate esters with the various eluents. These, in turn, are needed to plan the separation intelligently.

Methods

Five methods were used:

(1) *Centrifuge.* Short columns were prepared in centrifuge tubes. The eluent was drained to the upper level of the resin; the tube was weighed, centrifuged, and reweighed. The loss in weight represents the interstitial solution. Corrections were applied (*a*) for the liquid removed from the filter disc during centrifugation and (*b*) for the interstitial solution (3% of the bed volume) that clings to the resin even after centrifugation.

(2) *Break-through experiment with polystyrene sulphonic acid.* A column was equilibrated with the eluent to be studied containing 0·001*N* linear polystyrene sulphonic acid. Then the same eluent, free of the polystyrene sulphonic acid, was passed through the column. Fractions of the effluent were analysed to locate the break-through of the polymer-free eluent. This break-through was sharp. The volume of effluent collected when the concentration of the polystyrene sulphonic acid was 0·0005*N* was taken as the interstitial volume. A correction was applied for the volume of liquid in the pores of the filter disc and clinging to the inside walls of the tube below the filter. Polystyrene sulphonic acid was used for this purpose because its large molecular size prevents it from penetrating into the resin beads.[12]

(3) *Determination of interstitial polystyrene sulphonic acid.* A column was equilibrated with the eluent in question containing 0·001*N* polystyrene sulphonic acid. After draining the eluent to the upper level of the resin, the same eluent without the polyelectrolyte was passed through the column until all the polyelectrolyte was removed. The polyelectrolyte in the effluent was determined. This quantity, in milliequivalents, divided by the normality of the polyelectrolyte, gives the interstitial volume. A correction was applied as in the foregoing method.

(4) and (5) *Analogous methods with sodium polyphosphate.* Methods (4) and (5) are analogous to methods (2) and (3), respectively, except that sodium polyphosphate was employed as the polyelectrolyte. Also, in order to avoid degradation of the polyphosphate, the hydrochloric acid was omitted from the eluents.

Elution

The preparation of columns for ion-exchange separation has been described.[13] The resin, having a capacity of 3·82 meq per g, was equilibrated with the eluent, 4·0*M* in LiCl and 1·0*M* in HCl, by passing 1 litre of this solution through the column. The eluent was then drained to the top of the resin bed. The height of the resin column at this point was 61·8 cm. A sample of 1·00 ml was pipetted on to the top of the resin bed and was allowed to drain into the resin. At this point, collection of the effluent was initiated. The sample was then completely washed into the resin with the aid of three small portions of the first eluent (3–4 ml). After each addition the solution was permitted to drain into the resin. All eluent changes were made after draining the previous eluent completely into the resin bed. The column was maintained at a temperature of 50 ± 2°. The hydrostatic head of the eluent was adjusted (1·5 metres) so as to give an initial flow rate of 0·11 cm per min. Small fractions (2·76 or 3·10 ml) were collected with the aid of a siphon pipette[14] and a Misco fraction collector.

Analysis of eluate fractions

The procedure used involved the conversion of the organophosphorus acids to orthophosphate, and the determination of the resulting orthophosphate by the molybdovanadate method.[15–17]

The investigation of Kolmerten and Epstein[18] indicated the vital role played by the ratio of the chloride ion to sodium hydroxide concentrations in the persulphate oxidation of organophosphorus compounds. They used sodium sulphite to destroy the excess persulphate that remained after 1 hour of heating. This step was eliminated in this work by extending the period of heating to 2 hours. The phosphovanadomolybdate method, originally proposed by Misson,[17] was used to determine the concentration of the orthophosphate.

Each fraction, containing 2·76 or 3·10 ml of a solution 4·0*M* in LiCl and 1·0*M* in HCl plus no more than 0·03 mmols of phosphorus, was treated with 1·0 ml of 18*M* sodium hydroxide and 2·0 ml of 1·0*M* ammonium persulphate. Distilled water was added to bring the final volume to approximately 20 ml. The contents of each test-tube were thoroughly mixed, and the test-tubes were placed in a

beaker of boiling water. The samples were digested for a period of 2 hr. Fractions that contained 1·0*M* HCl or water, plus no more than 0·03 m mols of phosphorus, were treated in the same way except that only 0·5 ml of 18*M* sodium hydroxide was used. The contents of each test-tube were then quantitatively transferred to a 100-ml volumetric flask with the aid of 50 ml of 0·3*M* nitric acid. Exactly 25 ml of vanadomolybdate reagent, prepared according to the method of Barton,[15] were pipetted into each flask. The solutions were then diluted to the mark with distilled water, and the contents of each flask were thoroughly mixed. The absorbance at 400 mμ,[15,16] versus a blank prepared in the same manner, was determined after a 2-hr development period. All absorbance measurements were made with a Beckman DU spectrophotometer with 1-cm Corex cells. Calibration curves were prepared according to the method proposed by Goudie and Rieman.[19]

RESULTS AND DISCUSSION

The interstitial volumes

Table I gives a summary of the determinations of the relative interstitial volumes, *i.e.*, the ratio of the interstitial volume to the bed volume.

TABLE I.—RELATIVE INTERSTITIAL VOLUME OF DOWEX 50-X4 (325 mesh, 4·03 meq per g)

Eluent	0·0*M* LiCl 1·0*M* HCl	2·0*M* LiCl 1·0*M* HCl	4·0*M* LiCl 1·0*M* HCl	6·0*M* LiCl 1·0*M* HCl	8·0*M* LiCl 1·0*M* HCl
Mean relative interstitial vol.	0·325	0·335	0·346	0·355	0·380

The standard deviation never exceeded 0·20. Thus, these results have about the same precisions as those reported elsewhere.[12] As is to be expected from the fact that the resin shrinks and becomes less deformable in concentrated LiCl, the interstitial volume increases with increasing concentration of eluent.

Changes in column height

The volume of a bead of ion-exchange resin increases with decreasing concentration of electrolytes in the eluent. When the eluent was changed from a solution 4·0*M* in LiCl and 1·0*M* in HCl to 1·0*M* HCl, the first effect of this swelling was a decrease in the interstitial volume and hence in the flow rate; the rate diminished to about one-half of its original value. Later, the resin bed expanded and the column height rose to a steady value of 77·0 cm. During this expansion, the flow rate gradually increased to about its original value. The second change of eluent from 1·0*M* HCl to pure water caused another gradual increase in column height to 99·5 cm without great changes in the flow rate.

Temperature effect

Resins of lower capacities do not swell as much as resins of normal capacities.[8] Since the former have less internal water, diffusion within these resins is restricted. Thus slow flow-rates would be necessary to ensure the attainment of equilibrium conditions and symmetrical elution graphs. Higher temperatures increase the diffusion rates within the resins, thereby permitting higher flow-rates. Temperatures above 50° are not desirable because of the formation of air bubbles in the ion-exchange columns.

Flow-rates between 0·03 and 0·20 cm per min resulted in symmetrical elution curves. Flow-rates greater than 0·20 cm per min were not used because some of the elution graphs began to exhibit tailing. Flow-rates below 0·03 cm per min are not convenient.

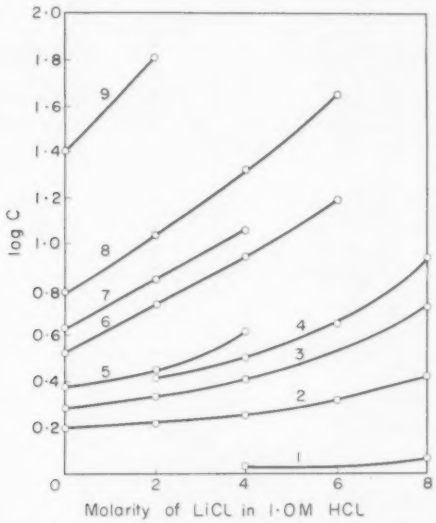

FIG. 1.—Plots of log C *vs.* molarity of LiCl in 1·0M HCl with Dowex 50-X4, 4·03 meq per g.
1. H_3PO_4; 2. $CH_3PO(OH)_2$; 3. $EtPO(OH)_2$; 4. $HOPO(OMe)_2$; 5. $PrPO(OH)_2$;
6. $HOPO(OEt)_2$; 7. $BuPO(OH)_2$; 8. $HOPO(OPr)_2$; 9. $HOPO(OBu)_2$.

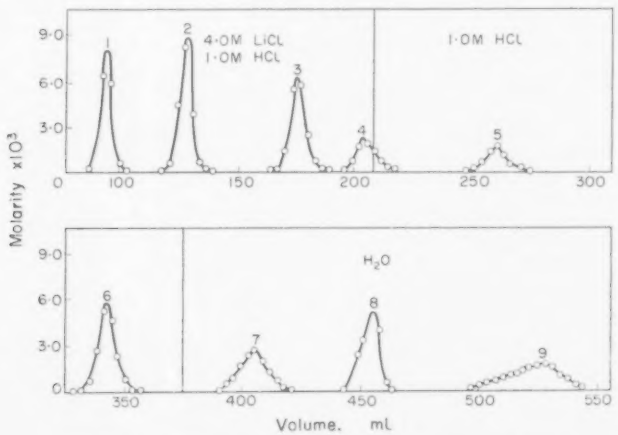

FIG. 2.—Separation of a nine-component mixture.
61·8 cm × 2·76 cm² Dowex 50W-X4, 325 mesh, 3·82 meq per g.
The numbers correspond to the compounds listed in Fig. 1.

Results of analysis of known mixtures

Fig. 1 demonstrates that the plots of log C versus concentration of the lithium chloride are not linear. This is to be expected since equation (2) is applicable only if the resin remains in the same ionic form.[9] This is not the case with the results of Fig. 1; the mole fraction of lithium resin decreases with decreasing LiCl in the eluent.

Fig. 2 reveals the quantitative separation of the nine compounds under investigation. No theoretical explanation can be given by the authors for the heading exhibited by $(BuO)_2PO(OH)$. Table II lists the recoveries obtained from three separate analyses. The recoveries are within the experimental limits observed in the determination of known concentrations of organophosphorus compounds under the same condition.

Acknowledgments—The authors are deeply grateful to the U.S. Army Chemical Center for the generous financial and material assistance that made this investigation possible. They would also like to express their sincere thanks to The Dow Chemical Company for supplying the special low-capacity resin.

Zusammenfassung—Versuche einige Phosphorsäure durch Gaschromatographie und Anionenaustauschchromatographie zu trennen waren erfolglos. Die vorliegende Arbeit beschreibt eine quantitative Trennungsmethode durch Aussalzchromatographie an einem speziellen Harz Dowex 50-X4 mit niederer Kapazität.

Résumé—Une tentative de séparation de différents acides phosphoreux par chromatographie de gaz et d'échanges anioniques n'a pas réussi. Cet article décrit une méthode quantitative de séparation par chromatographie d'exclusion d'ions sur des résines spéciales Dowex 50-X4 de faible capacité.

TABLE II.—ANALYSIS OF KNOWN MIXTURES

Mixture no.	1			2			3		
Compound	Taken, mmoles.	Found, mmoles.	% recovery	Taken, mmoles.	Found, mmoles.	% recovery	Taken, mmoles.	Found, mmoles.	% recovery
H_3PO_4	0·0362	0·0378	104	0·0362	0·0375	103	0·0422	0·0401	95
$MePO(OH)_2$	0·0481	0·0481	100	0·0481	0·0505	105	0·0561	0·0556	99
$EtPO(OH)_2$	0·0444	0·0415	94	0·0444	0·0446	100	0·0513	0·0495	97
$HOPO(OMe)_2$	0·0177	0·0168	95	0·0177	0·0174	98	0·0206	0·0220	107
$PrPO(OH)_2$	0·0140	0·0139	99	0·0140	0·0145	103	0·0163	0·0165	101
$HOPO(OEt)_2$	0·0484	0·0454	94	0·0484	0·0520	108	0·0564	0·0532	94
$BuPO(OH)_2$	0·0331	0·0286	86*	0·0331	0·0347	105	0·0386	0·0379	98
$HOPO(OPr)_2$	0·0379	0·0383	100	0·0379	0·0395	104	0·0442	0·0452	102
$HOPO(OBu)_2$	0·0379	0·0367	97	0·0379	0·0398	105	0·0442	0·0453	102
Mean			98			103			99
Standard deviation			4			3			4

* A failure of the automatic fraction collector caused the loss of eluate from $U = 398$ to $U = 428$. Since this portion contained some $BuPO(OH)_2$, the recovery of this compound is low. This value has been excluded from the mean and standard deviation.

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TITRIMETRIC DETERMINATION OF TITANIUM^{III} WITH SODIUM METAVANADATE—I

USE OF NEUTRAL RED, PHENOSAFRANINE OR SAFRANINE-T AS REDOX INDICATORS

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Summary—Conditions have been developed for the titrimetric determination of titanium^{III} with sodium metavanadate in a hydrochloric acid medium at room temperature, using neutral red, or phenosafranine, or safranine-T as redox indicators. A study of the indicator reactions has shown that while the reduced dye is rapidly oxidised by a trace of sodium metavanadate, the oxidised dye is only very slowly reduced by titanium^{III} in a hydrochloric acid medium. The reaction is, however, markedly accelerated by oxalic acid even at room temperature. This catalysis enables the satisfactory functioning of any of these dyes as internal indicators for the titration of titanium^{III} with vanadium^{V}. The colour of the dye which is discharged by titanium^{III} in a hydrochloric acid + oxalic acid medium is sharply restored when all of the titanium^{III} is oxidised to titanium^{IV}. In this titration the vanadium^{V} is reduced to vanadium^{III}. Iron^{II} and low concentrations of vanadium^{III} do not interfere in the titration. Methylene blue cannot be used as a redox indicator in this titration.

SMITH and Kurtz[1] employed cerium^{IV} sulphate for the differential visual titration of titanium^{III} and iron^{II} in a carbon dioxide atmosphere using methylene blue and ferroïn as indicators for the first and second parts of the titrations. Shippy[2] carried out the same determination with potassium permanganate. The mixture was first titrated at 60° in a carbon dioxide atmosphere with potassium permanganate using methylene blue as indicator, then titrated at room temperature using ferroïn as indicator. The first titre gives a measure of titanium^{III} and the second titre gives a measure of iron^{II}. Syrokomskii and Silaeva[3] titrated titanium^{III} with cerium^{IV} sulphate solution, using cacotheline as indicator. They stated that the titration could be carried out even in the presence of air, if the mixture is treated with 15 ml of saturated ammonium sulphate solution or 10 ml of acetic acid. They believe that the complexes formed by titanium^{III} with ammonium sulphate or acetic acid are suffiently stable to resist oxidation by atmospheric oxygen during the titration. Wehber, Johannsen and Heydecke[4] carried out the determination of titanium^{III} and iron^{II} in a mixture, employing potassium dichromate as an oxidimetric titrant and cacotheline and the sodium salt of *N*-methyldiphenylamine sulphonic acid as redox indicators. From a survey of the literature, it appears that the titrimetric determination of titanium^{III} has not so far been made with sodium metavanadate using redox indicators. When vanadium^{V} solution is added slowly to a titanium^{III} solution, the vanadium^{V} is reduced to vanadium^{III}:

$$VO_2^+ + 2Ti^{3+} \rightarrow V^{3+} + 2TiO^{2+} \quad (1)$$

Although vanadium^{IV} may appear as an intermediate, it will be reduced further to vanadium^{III}. The vanadium^{III} is capable of reacting further with vanadium^{V}:

$$V^{3+} + VO_2^+ \rightarrow 2VO^{2+} \quad (2)$$

The end of (1) can be detected by indicators having such low redox potentials that their reduced forms are easily oxidised by vanadium^{IV}. We have carried out the titration of titanium^{III} using neutral red, phenosafranine and safranine-T as redox indicators. According to Tomiček,[5] these indicators have normal potentials of 0·34 V, 0·25 V and 0·289 V, respectively, at pH 7 and a temperature of 30°. From the results presented in Table I, it will be evident that the speed of reduction of any one of these dyes by titanium^{III} in a 1·0*N* hydrochloric acid medium is very slow at room temperature. The reduction of the dye by titanium^{III} is, however, much accelerated by a small concentration of oxalic acid. It has therefore been found possible to carry out titrations of titanium^{III} with sodium metavanadate in a hydrochloric acid medium at room temperature, using any one of these dyes as an internal indicator in an inert gas atmosphere.

EXPERIMENTAL

Reagents

Titanium^{III} solution: The sample of titanium^{III} chloride employed in this investigation was of Analytical Reagent quality supplied by May and Baker, London. It was tested and found to be free from iron^{II}. A 0·05*N* solution of titanium^{III} in 2*N* hydrochloric acid solution was prepared from this sample and stored in the customary manner in an atmosphere of nitrogen. It was standardised by adding an aliquot to an excess of iron^{III} alum solution and titrating the iron^{II} formed against standard potassium dichromate solution, using diphenylbenzidine as internal indicator.

Sodium metavanadate solution: A 0·05*N* solution was prepared from B.D.H. AnalaR-grade ammonium metavanadate, by dissolving the requisite quantity of the sample in 300 ml of water and heating with a slight excess of sodium carbonate until all the ammonia was driven off. The solution was cooled and made up to 1 litre, and was standardised against a solution of Mohr's salt, which in turn had been standardised against a standard solution of potassium dichromate.

Indicator solutions: A 0·1% aqueous solution of each indicator was prepared from a sample supplied for use as a biological stain. A 0·1-ml portion of this solution was added to 50 ml of the titration mixture. In 1·0*N* hydrochloric acid the colours of the three indicators (neutral red, phenosafranine and safranine-T) are found to be purple, reddish-purple and red, respectively. These change to colourless when reduced to the leuco state. Fresh solutions of the indicators should be used. An aged sample of phenosafranine gives considerable trouble in the detection of the true end-point.

RESULTS AND DISCUSSION

Influence of oxalic acid on the speed of reduction of neutral red, phenosafranine, and safranine-T by titanium^{III}

Fifty ml of 1*N* hydrochloric acid containing 0·1 ml of the indicator solution were transferred to a vessel fitted with a three-holed stopper. Through the central hole passed a microburette connected to the storage bottle containing titanium^{III}, and the two other holes carried the inlet and outlet tubes for passing carbon dioxide. Carbon dioxide was passed through the vessel for about 10 min, and 0·05 ml of about 0·05*N* titanium^{III} chloride solution was then added from the microburette. The time taken for the discharge of the indicator colour was noted. The observations are recorded in Table I.

It is evident from Table I, that the speed of reduction of the indicator by titanium^{III} is very slow and that it is markedly accelerated by oxalic acid. The formal potential of the Ti^{IV}/Ti^{III} couple in 1*N* hydrochloric acid at 28° was found to be 0·027 V against the normal hydrogen electrode. The formal potential was not altered by the addition of oxalic acid at concentrations lying between 0·005 to 0·100 moles per litre to a solution containing titanium^{III} and titanium^{IV} each at 0·005*M* concentration. Although no change in potential was observed on the addition of oxalic acid to the titanium^{III}–titanium^{IV} mixture, the mixture developed a yellow-brown colour even in 1·0 *N* hydrochloric acid. This indicates the formation of a complex which is quite

TABLE I. INFLUENCE OF OXALIC ACID ON THE SPEED OF REDUCTION OF NEUTRAL RED, PHENOSAFRANINE AND SAFRANINE-T BY TITANIUM^{III} IN 1·0*N* HYDROCHLORIC ACID

Concentration of oxalic acid, *moles per litre*	Time taken for the discharge of the colour of the dye, *sec*		
	Neutral red	Phenosafranine	Safranine-T
Nil	840	840	840
0·005	160	100	120
0·005	60	40	50
0·010	15	8	10
0·020	5	2	5
0·050	immediate	immediate	immediate
0·100	immediate	immediate	immediate

stable to hydrochloric acid. Pecsock[6] has already reported that the titanium^{III}–oxalate complex is yellow and has the composition titanium^{III}:oxalate = 1:2, and that the titanium^{IV}–oxalate complex is colourless. Our observation that there is no change of potential on adding oxalic acid to the titanium^{III}-titanium^{IV} mixture leads to the conclusion that both the oxalate complexes of titanium^{III} and titanium^{IV} have nearly the same stability constants. A similar conclusion appears to have been arrived at by Pecsock[6] from his polarographic studies. It is very significant that oxalic acid exerts a marked accelerating action on the reduction of the dye by titanium^{III}, although it does not change the redox potential of titanium^{III}. The transition potentials of the three indicators were found to be +0·1 V, +0·16 V and +0·17 V for neutral red, phenosafranine and safranine-T, respectively. These are the potentials at which the indicator colour is discharged in 1·0*N* hydrochloric acid in the presence of oxalic acid and in an atmosphere of carbon dioxide at 28°. Under the conditions of titration recommended below, the indicator correction has been found to be negligible.

Recommended procedure

Twenty-five ml of 2*N* hydrochloric acid, 10–15 ml of 0·5*M* oxalic acid and 0·1 ml of 0·1 % indicator solution are transferred to a titration flask fitted with a four-holed stopper. Through two holes pass the inlet and outlet tubes for passing carbon dioxide and through the other two holes pass the microburette containing sodium metavanadate solution and the microburette attached to the titanium^{III} reservoir. A stream of carbon dioxide is passed through the mixture for 10 min to free it from air. An aliquot of the titanium^{III} solution (about 3–5 ml of about 0·05*N* solution) is then added to the mixture. The mixture is titrated with sodium metavanadate solution while carbon dioxide continues to pass rapidly. The end-point of the titration is sharply indicated by the appearance of the original colour of the dye. The progress of the titration is also indicated by the gradual disappearance of the yellow-brown colour of the titanium^{III}–oxalate complex, the titanium^{IV}–oxalate complex being colourless. In dealing with dilute solutions, the blue-green colour of vanadium^{III} does not mask the strong purple colour of neutral red, the reddish-purple colour of phenosafranine or the red colour of safranine-T. In titrations of titanium^{III} solutions of higher concentration than that indicated above, this difficulty arises.

A large number of titrations have been made under the conditions recommended and some typical results are presented in Table II. In this titration the vanadium^{V} is reduced to vanadium^{III}. Hence the equivalent weight of sodium metavanadate is equal to half the formula weight.

TABLE II. VANADAMETRIC DETERMINATION OF TITANIUM^{III}

Indicator	Amount of titanium^{III} taken, *millimoles*	Amount of titanium^{III} found, *millimoles*
Neutral red	0·8463	0·8458
	0·6356	0·6361
	0·5328	0·5324
	0·2664	0·2659
	0·2234	0·2232
Phenosafranine	0·9486	0·9482
	0·7434	0·7430
	0·4743	0·4748
	0·3665	0·3656
Safranine-T	0·8764	0·8766
	0·6822	0·6824
	0·4368	0·4362
	0·2436	0·2440

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Variation of hydrochloric acid concentration

The acid concentration of the titration mixture can be varied from 1*N* to 3*N* hydrochloric acid without affecting the accuracy of the titration. All three indicators have a purple colour in 3·0*N* hydrochloric acid which is slightly different from the colours in 1·0*N* hydrochloric acid.

Advantages of the vanadametric procedure

As the transition potentials of neutral red, phenosafranine and safranine-T are lower than the redox potentials of vanadium^{III} and iron^{II}, it is obvious that titanium^{III} can be titrated with sodium metavanadate in the presence of vanadium^{III} and iron^{II} using these indicators. Vanadium^{III} and iron^{II} interfere in the titration of titanium^{III} with sodium metavanadate if indicators like diphenylbenzidine, *N*-phenylanthranilic acid and ferroïn are employed. A large number of titrations of titanium^{III} have been made with sodium metavanadate, using neutral red, phenosafranine or safranine-T in the presence of iron^{II} or vanadium^{III} under the recommended conditions, and these have shown that iron^{II} and vanadium^{III} do not interfere. The vanadium^{III} should not be present in such a concentration as to mask the colour of the indicator.

Potassium dichromate has been tried as the oxidimetric titrant in place of sodium metavanadate but the results were found to be high and erroneous, presumably because of the reaction between titanium^{III} and chromium^{VI} inducing a reaction between oxalic acid and chromium^{VI}.

Zusammenfassung—Bedingungen zur titrimetrischen Bestimmung von Titan(III) mit Natriummetavanadate in salzsaurer Lösung, bei Zimmertemperatur und unter Verwendung von Neutralrot, Phenosafranin oder Safranin T als Redoxindicator wurden entwickelt. Es wurde gefunden, dass der reduzierte Indicator sehr rasch durch Metavanadat oxydiert wird, während die oxydierte Form nur sehr langsam durch Titan(III) reduziert wird. Die letztere Reaktion wird jedoch durch Zusatz von Oxalsäure wesentlich beschleunigt und das selbst bei Raumtemperatur, sodass jeder der erwähnten Farbstoffe als Indicator verwendet werden kann. Die Farbe der Indicatoren verschwindet in Salz-Oxalsäuremedium auf Zugabe von Titan(III), wird jedoch rasch wiederhergestellt, wenn alles Titan

zur vierwertigen Stufe oxydiert ist. In dieser Titration wird Vanadin(V) zu Vanadin(III) reduziert. Eisen(II) und kleine Mengen von Vanadin(III) stören die Bestimmung. Methylenblau kann als Indicator nicht verwendet werden.

Résumé—Les auteurs ont mis au point les conditions du dosage titrimétrique du titane(III) par le métavanadate de sodium en milieu acide chlorhydrique à la température ambiante, en utilisant le rouge neutre, la phénosafranine ou la safranine T comme indicateurs d'oxydo-réduction. Une étude des réactions de l'indicateur a montré que, tandis que le colorant réduit est oxydé rapidement par une trace de métavanadate de sodium, le colorant oxydé est réduit seulement très lentement par le titane-(III) en milieu acide chlorhydrique. Cependant, la réaction est notablement accélérée par l'acide oxalique, même à la température ambiante. Cette catalyse permet à n'importe lequel de ces colorants de fonctionner comme indicateur interne pour le dosage du titane(III) par le vanadium(V). La couleur du colorant, qui est masquée par le titane(III) en milieu acide chlorhydrique-acide oxalique, réapparaît nettement quand tout le titane(III) est oxydé en titane(IV). Dans le titrage le vanadium(V) est réduit en vanadium(III). Le fer(II) et de faibles concentrations de vanadium(III) ne gênent pas. Le bleu de méthylène ne fonctionne pas comme indicateur interne.

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PRELIMINARY COMMUNICATION

Die Bestimmung von Fluor in Mineralwässern mittels Zr-Xylenolorange

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Zur Bestimmung kleiner Mengen von Fluor nützt man meistens ihre Fähigkeit aus, färbige Chelate oder Komplexe einiger Metalle zu zersetzen. Aus der Tabelle ist ersichtlich, dass der Einfluss der Komponenten, welche bei dieser Bestimmung stören, klein ist, wenn man zu diesem Zweck Zr-Xylenolorange benützt. Im Vergleich mit der das erstemal von Megregian[1] veröffenslichten Zr-Eriochromcyanin-Methode, welche für eine der besten gegenwärtigen Fluorbestimmungen gehalten wird,[2] ist in der neu vorgeschlagenen Methode z.B. der Einfluss von Phosphaten um zwei und der Einfluss der Sulphate um mehr als eine Grössenordnung kleiner. Ausserdem ist die Zr-Xylenolorange-Methode um eine halbe Grössenordnung empfindlicher. Ausführlichere Angaben werden später veröffentlicht.

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Tabelle I.—Der Einfluss der hauptsächlich störenden komponenten in 1,2 n HCl

μg/50 ml	Einfluss %
10 F^- + 5000 PO_4^{3-}	0
10 F^- + 50 Al^{3+}	0
10 F^- + 2000 Fe^{3+}	0
6 F^- + 6000 SO_4^{2-}	+15
10 F^- + 10000 SO_4^{2-}	+12*
16 F^- + 16000 SO_4^{2-}	+8

* Bei dem Gebrauch verschiedener Präparate von Xylenolorange (der Fma. Chemapol) wurde der Einfluss von 6–24% festgestellt. Grössere Fehler entstehen wahrscheinlich infolge der Zersetzung von Xylenolorange. Wenn man nämlich die Lösung des Präparates mit kleinstem Sulphateinfluss mit ultraviolettem Licht beleuchtete, verminderte sich das Absorptionsmaximum (440 mμ) der Lösung und der Einfluss der Sulphate erhöhte sich.

Der Hauptgrund des kleineren störenden Einflusses fremder Ione in der neu vorgeschlagenen Methode ist die grössere Stabilität des Chelates von Zirkon mit einem Farbstoff, welches zwei N,N-di(carboxymethyl)-aminomethyl Gruppen hat. Diese Stabilität ermöglicht die Bestimmung von Fluor in einem relativ stark sauren Milieu, welches z.B. den Ion AlF^{2+} zersetzt, welcher bei der Fluorbestimmung schon bei gleicher Menge von Aluminium und Fluor oft beträchtliche negative Fehler verursacht.[3] Beim Gebrauch stabiler Chelate äussert sich auch am besten der Unterschied in der Festigkeit der Bindung von Zirkon mit z.B. Fluorid und Sulphat. Wenn im Gegenteil die Bindung von Zirkon mit dem Farbstoff schwächer ist als die zwischen Zirkon und Sulphat, ist die Destruktionswirkung der Sulphate und Fluoride gegenüber einem solchem Chelat praktisch dieselbe.

ARBEITSVORSCHRIFT

Wenn das analysierte Naturwasser ungefähr 1 mg F/l enthält, werden 10 ml der Probe in einen 50 ml Messkolben mit 10 ml Zirkon-Lösung* pipettiert. Nach einer 20 Min. dauernden Erwärmung

* Bei der Herstellung der Zirkon-Lösung wurden 30,0 mg $ZrOCl_2.8\ H_2O$ in etwa 40 ml dest. Wasser aufgelöst und einer ausgekühlten verdünnten Salzsäure (500 ml konc. HCl + ca 400 ml H_2O) beigemischt und auf 1000 ml aufgefüllt. Damit die Polymerisation der Zirkonionen ausgeschlossen wird, ist es nicht ratsam, die Temperatur der Lösung unter 20° sinken zu lassen.

bei etwa 60° und einer 40 Min. dauernden Abkühlung der Lösung werden 2,00 ml einer 0,20% wässerigen Lösung von Natrium-Xylenolorange beigegeben und das Volumen der Lösung auf 50 ml aufgefüllt. Nach ungefähr 1 St. werden die Lösungen in Küvetten von 4 cm Messlänge bei 540 mμ gegenüber einer gleich zubereiteten Bezugslösung mit 20 μg F/50 ml photometriert.

Der summare Fluorgehalt der Proben wird mittels einer Eichkurve ausgewertet, deren Verlauf man inmitten jeder Bestimmungsserie mit Hilfe einiger Eichlösungen und mittels eines Korrektionsnomogrammes für den Sulphatgehalt bestimmt.

Die Messungen wurden mit Hilfe des Spektrophotometers Uvispek der Fma Hilger durchgeführt.

Ebenfalls wird die Ausnützung weiterer der Xylenolorange ähnlicher Farbstoffe wie z.B. Sarkosinkresol-Rot, Methyl-, Butylthymol-Blau usw. und auch Arsenazo III verfolgt.

ROMAN VALACH

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Zusammenfassung—Die neue vorgeschlagene Methode, welche die Entfärbung des Chelates von Zirkon mit Xylenolorange im Milieu einer beiläufig 1,2*N* Salzsäure ausnützt, ermöglicht eine schnelle Bestimmung von Fluor in Mineralwässern und anderen Materialen mit hohem Gehalt an Phosphaten, Sulfaten, Eisen (III) und Aluminium und anderen Ionen.

Summary—The method proposed, based on the decolorisation of the zirconium–Xylenol Orange chelate in a 1·2*N* hydrochloric acid medium, permits rapid determination of fluorine in mineral waters and other materials containing relatively large amounts of phosphate, sulphate, aluminium, iron^{III} and other ions.

Résumé—Le dosage du fluorure est basé sur la décoloration du chélate zirconium-xylénolorange en milieu acide chlorhydrique environ 1,2*N*. Cela permet de doser rapidement le fluor dans les eaux minérales et dans d'autres produits contenant de plus grandes quantités de phosphate, sulfate, aluminium, fer ferrique et autres ions.

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Talanta, 1961, Vol. 8, pp. 445 to 449. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Precipitation from homogeneous solutions of mixed solvents

(*Received* 16 *January* 1961; *Accepted* 27 *February* 1961)

THE literature pertaining to methods of achieving precipitation from homogeneous solution has been carefully reviewed by Gordon, Salutsky and Willard.[1] A study of this compilation reveals that past procedures may be broadly classified into one of two groups. One of these involves the direct *in situ* generation of the precipitating ion by a controlled reaction, usually hydrolysis; and the other is an indirect method which utilises a gradual change of pH to decrease the solubility of the desired compound slowly. Although the precipitant may be a general reagent capable of the precipitation of several ions, serious limitations exist in the application of either of these methods. In the first case the generation reaction usually has a high pH dependence and thus the acidity of the solution must be within a specific range in order to achieve the required rate of precipitation. In the second case the use of a pH change to effect the precipitation results in the precipitation of all salts insoluble over the pH range employed. In neither case is one permitted a free choice of the pH required for selective precipitation.

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This project represents an attempt to arrive at a method whereby a general precipitating agent may be used to effect precipitation from an initially homogeneous solution of any desired pH. The general principle of the procedure involves the use of an organic precipitant which is added to a mixture of the solution containing the ion to be precipitated and a water-miscible organic solvent. Then, after the addition of the buffer, the organic solvent is removed by a slow volatilisation and precipitation of the desired compound at a pre-selected pH is permitted. That such a process should yield the desired increase in crystallinity, with its associated increase in ability to separate similiar species, is borne out by recently reported work of Firsching[2] and by an earlier paper by Wilson and Wilson.[3]

The present authors have shown that this method may be successfully employed for precipitating aluminium^{III} 8-quinolinate from a homogeneous acetone-water mixture to which all the requisite components, including buffering reagents, have been added. The procedure employed was to mix in a 250-ml beaker exactly 10 ml of an aluminium^{III} solution and 50 ml of distilled water. To this mixture were then added 60 ml of acetone, 4 ml of 5% 8-hydroxyquinoline in 2*N* acetic acid, and 40 ml of 2*N* ammonium acetate. The reaction mixture was placed on a water bath at 70°–75° and left uncovered for 3 hr. Visible precipitation began after about 15 min. At the end of the evaporation period the beakers were removed from the bath, allowed to cool, and filtered through medium-porosity sintered-glass crucibles. The precipitates were washed three times with distilled water and dried for 3 hr at 135°–140°. The product was weighed as anhydrous $Al(C_9H_6ON)_3$.

The aluminium^{III} solution was prepared from $KAlSO_4 \cdot 12H_2O$ so that 10 ml contained 10·06 ± 0·03 mg of Al^{III} as shown by the analysis of ten samples by the method of Olson, Koch and Pimentel.[4] When the above procedure was followed, the Al^{III} recovered from ten samples of 10 ml each was 10·04 ± 0·04 mg. The precipitates obtained were highly crystalline and were very easily filtered and washed.

Using a similar procedure, samples containing 10 mg of Mg^{II} have been analysed with good precision and accuracy, but with little improvement over conventional methods in the crystallinity of the precipitates formed or in the ease of filtering and washing. Precipitates obtained by both the evaporation method and the usual method of direct addition are grainy and easily handled.

In the case of zinc^{II} even large amounts of acetone fail to retard precipitation longer than about 1 min after the addition of the buffer solution. A co-precipitation study of magnesium^{II} 8-quinolinate on zinc^{II} 8-quinolinate was made, and the results obtained were essentially identical to those of Moyer and Remington.[5]

In addition to these studies, research on other solvent systems, cations, interfering ions and organic precipitating agents is in progress. Qualitative precipitations of aluminium^{III} 8-quinolinate from ethanol-water mixtures have been accomplished although the use of such mixtures entails evaporation times longer than those required when acetone is the organic component.

Acknowledgement—The authors gratefully acknowledge the financial support provided by the Research Corporation.

LESTER C. HOWICK®
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Summary—It has been shown that precipitation from homogeneous solutions of mixed solvents may be effected by the preferential volatilisation of one of the solvent components. The precipitation of aluminium^{III} 8-quinolinate from an acetone-water system yields quantitative results and a highly crystalline precipitate.

Zusammenfassung—Es wird gezeigt, dass Fällung aus homogener Lösung erzielt werden kann, indem man eine der Lösungsmittelkomponenten binärer Solventien bevorzugt verdampfen lässt. Die Fällung von Aluminiumoxinat ergibt quantitative Fällung aus Azeton-Wassermischung und ein schön kristalliner Niederschlag wird erzielt.

Résumé—Les auteurs montrent que la précipitation homogène à partir de solvants mixtes peut être effectuée par la volatilisation préférentielle de l'un des constituants du solvant. La précipitation du 8-quinolate d'aluminium dans le système eau-acétone donne des résultats quantitatifs et un précipité fortement cristallin.

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XXIX. Mitteilung über quantitative organische Analyse[1]

Eine automatische Methode zur Mikrobestimmung von Kohlenstoff, Wasserstoff und Stickstoff in organischen Substanzen

(*Received* 21 *December* 1960. *Accepted* 19 *January* 1961)

WIR haben gefunden, dass sich Mikroeinwaagen organischer Substanzen blitzartig verbrennen lassen, wenn man sie auf dem Schiffchen mit aktiven, durch thermischen Zerfall von Kobaltoxalat erhaltenem Co_3O_4 mischt. Die Verbrennung kann man in einigen Sekunden ohne Explosionsgefahr durchführen, wobei die Oxydation quantitativ verläuft, falls man die Produkte über eine Schichte von Co_3O_4 auf einem geeigneten Katalysatorträger[2] sowohl in Sauerstoff- als in Stickstoff- wie auch in Kohlendioxyd-Atmosphäre führt.

Damit wurden einerseits die Methoden zur gravimetrischen Bestimmung von Kohlenstoff und Wasserstoff sowie zur gasvolumetrischen Bestimmung von Stickstoff extrem vereinfacht und wesentlich beschleunigt,[3] anderseits konnten wir zur direkten Bestimmung der Verbrennungsprodukte

mittels Wärmeleitfähigkeit schreiten und damit den Weg zur Ausarbeitung von einfachen, volautomatischen Methoden der Elementeranalyse eröffnen.

Bei der blitzartigen Verbrennung verlassen die Verbrennungsprodukte das Verbrennungsrohr in einer Konzentrationswelle (siehe z.B. Abb. 1); zu Druckveränderungen kommt es im Messystem in kurzen Zeitintervellen und das noch früher, ehe die Front der Verbrennungsprodukte die Messzellen erreicht, sodass die Messung unbeeinflusst bleibt und die Bestimmung der Produkte ohne nötige Vorkondensation ermöglicht wird.

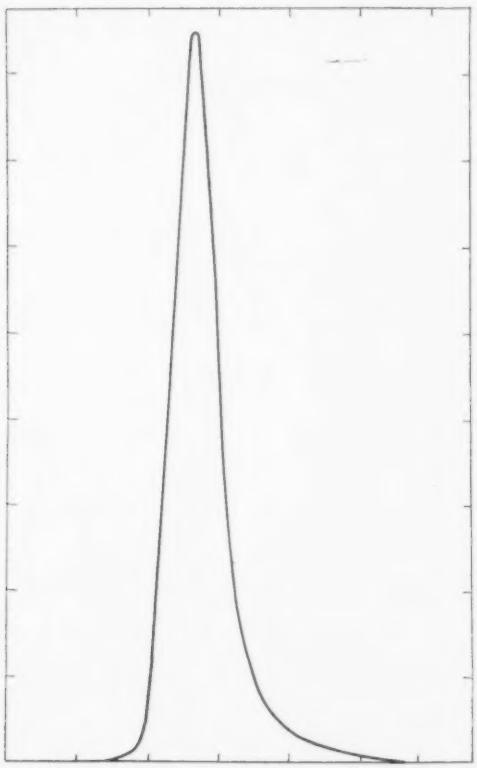

ABB. 1. Blitzartige Verbrennung von 1,203 mg des Acetanilids im Sauerstoffstrom. Die Konzentrationsaufnahme von CO_2.

Bei der Kohlenstoffbestimmung wird die eingewogene Substanz im Sauerstoffstrom verbrennt; nach Auffangen der Halogene, Schwefeloxyde, des Wassers und der Stickoxyde wird das Kohlendioxyd durch Messung der Änderung der Wärmeleitfähigkeit bestimmt, die mittels eines Schreibers registriert wird. Bei der Wasserstoffbestimmung wird die Substanz im Stickstoffstrom verbrannt, wobei die oxydierende Füllung des Verbrennungsrohres eine Schichte von CuO und Co_3O_4 auf Korund bildet in einer weiteren Schichte von Eisenfeilspänen kommt es zur Konversion von Wasser in Wasserstoff, der durch Änderung der Wärmeleitfähigkeit bestimmt wird. Die Bestimmung von Stickstoff wird im Kohlendioxydstrom in ähnlicher Weise ausgeführt, wie die Kohlenstoff und Wasserstoffbestimmung; als oxydierende Rohrfüllung dient Co_3O_4 und eine Schichte von CuO.

Die Auswertung und Berechnung erfolgte vorläufig durch Wägung der vom Schreiber aufgezeichneten ausgeschnittenen Flächen. In Zukunft soll ein Integrator verwendet werden. Die Eichungskurven wurden durch Analysen von Standardsubstanzen erhalten. Bisher wurden Resultate folgender Genauigkeit erreicht; Kohlenstoffbestimmung s m $\pm 0{,}46\%$; Wasserstoffbestim=ung s = $\pm 0{,}16\%$; Stickstoffbestimmung s = $\pm 0{,}27\%$. Einige Resultate befinden sich in Tabelle I.

TABELLE I.

Substanz	Formel (Mol. Gewicht)	Berechnet %	Gefunden %
		Wasserstoff	Wasserstoff
1-Chloranthrachinon	$C_{14}H_7O_2Cl$ (242,6)	2,91	2,89 2,93 2,98
Sacharose	$C_{12}H_{22}O_{11}$ (342,3)	6,48	6,26 6,62 6,66
Cholesterolazetat	$C_{29}H_{48}O_2$ (428,7)	11,29	11,44 11,33 11,10
		Kohlenstoff	Kohlenstoff
Sacharose	$C_{12}H_{22}O_{11}$ (342,3	42,11	42,32 42,60 41,82
Benzoesäure	$C_7H_6O_2$ (122,1)	68,84	68,03 68,06 69,64
Pikrinsäure	$C_6H_3O_7N_3$ (228,1)	31,45	31,14 31,18 32,06
		Stickstoff	Stickstoff
Antipyrin	$C_{11}H_{12}ON_2$ (188,2)	14,88	14,67 14,79 14,89
Acetanilid	C_8H_9ON (135,2)	10,36	10,55 10,15 10,61
Phenazetin	$C_{10}H_{13}O_2N$ (179,2)	7,82	7,60 8,03 7,69

Die Methoden sollen weiter durchgearbeitet werden, mit dem Ziel, ihre Genauigkeit zu steigern; es soll eine spezielle automatische Apparatur konstruiert werden und die Methode soll ebenfalls im Ultramikromassstab augeführt werden. Es wird auch die Überprüfung anderer Methoden der Endbestimmung geplant (z.B. mittels Ionisationsdetektoren), Ausarbeitung einer Methode zur gleichzeitigen Bestimmung von Kohlenstoff und Wasserstoff, möglicherweise die Verwendung anderer Trägergase.

Weitere Einzelheiten werden in der *Zeitschrift Collection Czechoslov. Chem. Commun.* angeführt werden.

EXPERIMENTELLER TEIL

Zur Bestimmung der Verbrennungsprodukte wurde ein semidiffuses Thermoelement verwendet, dessen Brücke mit 100–150 mA gespeist wurde (Bestimmung von Kohlenstoff und Wasserstoff) oder mit 200 mA (Bestimmung von Stickstoff), eingestellt mit einer Genauigkeit von ±0,2%; die graphische Aufzeichnung erfolgte mit dem automatischen linearen Schreiber "Honeywell" mit einem Skalenumgfang 10 mV.

Das pulverförmige Co_3O_4 wurde durch thermischen Zerfall von Kobaltoxalat bereitet,[4] weiter wurde dieser Katalysator auf Korund als Träger[1] verwendet. Die übrigen Reagentien waren die bei der Elementaranalyse üblichen (siehe z.B.[5]).

Zur Verbrennung und Erwärmung wurde die elektrische Universalapparatur verwendet, die schon früher beschrieben wurde.[6]

Kohlenstoffbestimmung

Das Verbrennungsrohr aus Quarz (Durchmesser 9 mm, Länge 320 mm) wird beginnend am Schnabel mit Silberwolle in einer Länge von 50 mm gefüllt; die Temperatur an dieser Stelle ist 600°.

Dann folgt eine 50 mm lange Schichte von Co_3O_4 auf Korund (Temperatur 700°). Die eingewogene Substanz (1–2 mg) wird mit 30–40 mg pulverförmigen Co_3O_4 bedeckt. Die Geschwindigkeit des Sauerstoffstromes ist 15 ml/min, die Zeitdauer der Bestimmung 5–7 Minuten.

Wasserstoffbestimmung

Im Quarzrohr (Durchmesser 9 mm, Länge 450 mm) befindet sich eine Schichte von Eisenspänen (120 mm), eine Schichte von CuO (30 mm) und Co_3O_4 auf Korund (50 mm) und wiederum eine Schichte von CuO (20 mm). Die ganze Füllung wird auf eine Temperatur von 650° erwärmt; die Geschwindigkeit des Stickstoffstromes ist 20 ml/Min., die Zeitdauer der Bestimmung 4–7 Minuten. Es wurde festgestellt,[7] dass es unter den gawählten Bedingungen zu einer 97–99% igen Konversion des Wassers zu Wasserstoff kommt.

Stickstoffbestimmung

Im Quarzrohr (Durchmesser 11 mm, Länge 600 mm) befindet sich eine Silberschicht (30 mm, Temperatur 550°), eine Schichte von Cu (40 mm, Temperatur 550°), eine Schichte von Co_3O_4 und CuO (50 resp. 200 mm, Temperatur 700°). Die eschwindigkeit des Kohledioxydstromes ist 10 ml/Min. Die Zeitdauer der Bestimmung 7–10 Minuten.

M. Večeřa

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Zusammenfassung—Eine Methode zur automatischen Bestimmung von C,H und N in organischen Verbindungen wird beschrieben. Die Methode arbeitet unter Ausnützung der Wärmeleitfähigkeit und verwendet Cobaltioxyd als Verbrennungskatalysator.

Summary—A method for the automatic determination of carbon, hydrogen and nitrogen in organic compounds is described. The method makes use of heat conductivity measurements, and Co_3O_4 is the combustion catalyst.

Résumé—L'auteur décrit une méthode automatique de microdosage du carbone, de l'hydrogène et de l'azote dans les composés organiques. La méthode dépend de la mesure de conductivité calorifique et utilise Co_3O_4 comme catalyseur de combustion.

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[2] M. Večeřa, D. Šnobl und L. Šynek, *Mikrochim. Acta*, im Druck.
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Talanta, 1961, Vol. 8, p. 450. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEW

Proceedings of the Symposium on the Chemistry of Co-ordination Compounds. Agra, India, February 7th and 8th, 1959. In three volumes: Part One, **General Survey,** pp. 148 + iii, Rs. 15.00: Part Two, **Valence Bond Considerations, Stereochemistry and Structure, Techniques and Methods of Investigation,** pp. 203 + ii, Rs. 25.00: Part Three, **Reactions, Stability and Thermodynamic Considerations, Stabilisation of Valence States, Analytical Applications, Miscellaneous,** pp. 302 + x, Rs. 35.00. Published by National Academy of Sciences, India, Lajpatrai Road, Allahabad, 1960.

THERE are about ninety papers in these volumes, of which twenty-three come from laboratories outside India, and the rest from various Indian research establishments. Most of the papers describe rather humdrum investigations by conventional methods, which will interest the reader chiefly to the extent that they happen to impinge on his own field of work. In the reviewer's opinion the main value of symposium publications of this sort lies not in the research reports, which could be and should be published in the ordinary chemical journals, but in the sprinkling of general review papers by outstanding contributors. Unfortunately the papers of this type given at the Agra symposium are not all in Part One, as might have been expected from the title, but are also to be found in Part Two, with a couple in Part Three. Among these the following deserve special mention: a paper from J. Chatt's laboratory on Pt^{II} complexes with acetylenic substances; V. Gutmann on the properties of arsenic trichloride and phosphorus oxychloride as solvents; D. G. Bradley on metal alkoxides; H. L. Nigam on bonding in carbonyl complexes; F. J. C. and Hazel Rosetti on stability constants; G. Mitra's papers on fluoro and hydroxyfluoro complexes, especially of boron; and the Presidential Address by P. Ray reviewing concisely the whole field of co-ordination chemistry.

While many of the papers in this publication are excellent and interesting, the general impression it gives is of a vast mass of not very closely related material, collected from almost every branch of inorganic chemistry. Consequently anyone who buys it for his private bookshelf is likely to end up reproaching himself for extravagance and poor judgement. It does, however, deserve a place as a work of reference in chemical libraries.

H. G. HEAL

Talanta, 1961, Vol. 8, p. 451. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

Tuesday-Thursday 10–12 *October* 1961: **Oak Ridge National Laboratory:** *Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology* and *Second Conference on Nuclear Reactor Chemistry*. Gatlinburg, Tennessee, U.S.A.

The Conference on Analytical Chemistry in Nuclear Reactor Technology will be devoted to improved methods and instruments for the analysis of many nuclear reactor materials and products. Papers are especially solicited on the following or related subjects: measurement of burnup of uranium or plutonium fuels; isotopic analysis; determination of gases in reactor materials; methods and instruments for on-line analyses; remote analysis of radioactive materials; non-destructive testing of nuclear fuel elements and other reactor materials; analysis of (a) beryllium, beryllium oxide, cermets containing beryllium oxide, (b) zirconium and niobium alloys, (c) heavy water, and (d) plutonium and plutonium-base fuels.

In addition to papers setting forth specific achievements, review papers critically evaluating the "state of the art" with respect to any of the foregoing subjects are solicited.

Authors are requested to submit an abstract of 200–400 words of their paper not later than 15 July, 1961, and at the same time to indicate the time required for their presentation (not to exceed 20 min).

Proceedings of the conferences are to be published. Manuscripts of papers for publication should be submitted prior to or at the time of the conferences.

Abstracts of papers and enquiries regarding the analytical chemistry section should be addressed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee, U.S.A.

Enquiries concerning accommodation or requests for reservations should be addressed to: Reservation Services, Chamber of Commerce, Gatlinburg, Tennessee, U.S.A.

The seventeenth Annual General Meeting of the Microchemistry Group of the Society for Analytical Chemistry was held at Burlington House, London, W.1, on Friday, 24 February 1961. The Chairman of the Group, Mr. F. HOLMES, presided.

The following were elected Officers of the Group for the forthcoming year:

Chairman: Mr. C. WHALLEY
Vice-Chairman: Miss M. CORNER
Hon. Treasurer: Mr. G. INGRAM
Hon. Secretary: Mr. D. W. WILSON, Chemistry Department, Sir John Cass College, Jewry Street, Aldgate, London, E.C.3.

Talanta, 1961, Vol. 8, p. 452. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Continuous coulometric titration of micro quantities of iron in water. TAKEO TAKAHASHI and HIROSHI SAKURAI. (29 *March* 1961).

Titrimetric analysis with chloramine-T—IV: The chloramine-T-iodide reaction. E. BISHOP and V. J. JENNINGS. (6 *April* 1961).

The use of ruthenium as a catalyst in redox titrations. C. J. KEATTCH. (6 *April* 1961).

Determination of alkali sulphides by direct titration. SÁNDOR A. KISS. (14 *April* 1961).

Untersuchung der Kationensorption aus Komplexanmedium-I: Chromatograpische Trennung des Calciums und Strontiums. PAVEL POVONDRA, ZDENĚK ŠULCEK, RUDOLF PŘIBIL und RICHARD STANGL. (18 *April* 1961).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—IV: Uranium. JON BORDNER, E. D. SALESIN and LOUIS GORDON. (19 *April* 1961).

Use of nickel phthalocyanine sulphonic acid as a redox indicator in cerimetry—I. G. GOPALA RAO and N. VENKATESWARA RAO. (20 *April* 1961).

5-Amino-2-benzimidazolethiol as a new analytical reagent—II: Spectrophotometric determination of rhodium, and the simultaneous determination of rhodium and palladium. J. G. SEN GUPTA. (27 *April* 1961).

Cerimetric determination of nickel phthalocyanine. N. VENKATESWARA RAO and G. GOPALA RAO. (27 *April* 1961).

Cerimetric determination of triphenylmethane dyes—I: Determination of crystal violet. G. GOPALA RAO and N. VENKATESWARA RAO. (27 *April* 1961).

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EIGHTIETH BIRTHDAY OF PROFESSOR HOBART H. WILLARD

Professor Hobart H. Willard receiving from Professor Louis Gordon (Regional Editor of *Talanta*) a blue leather-bound copy of the Willard Issue (*Talanta* 1961, **7**, Numbers 3/4) presented on 12 May 1961, on behalf of the publishers of the Journal, Pergamon Press Limited, on the occasion of his birthday celebration at Ann Arbor, Michigan. Professors Harvey Diehl and G. Frederick Smith, members of the Advisory Board of *Talanta*, are also in the picture.

(Photo by Talbot Studios, Ann Arbor, Michigan, U.S.A.)

Former students and associates of Professor Hobart H. Willard who were able to attend the birthday celebration.

Shown from left to right are:

Back row: Dwight Williams, J. J. Thompson.

Centre row: John Ross, Charles A. Horton, Lynne L. Merritt, Jr., R. B. Hahn, Edwin W. Goodspeed, R. R. Ralston, C. W. Zuehlke, Headlee Lamprey, Ross W. Moshier, Louis Gordon, Harvey Diehl, G. Frederick Smith.

Front row: A. J. Boyle, Frank L. Chan, Elmer Leininger, H. H. Willard, R. C. Gibson, R. K. McAlpine, Byron Soule.

(Photo by Talbot Studios, Ann Arbor, Michigan, U.S.A.)

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Talanta, 1961, Vol. 8, pp. 453 to 460. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF GERMANIUM WITH *p*-DIMETHYLAMINOPHENYLFLUORONE

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(*Received* 17 *October* 1960. *Accepted* 28 *December* 1960).

Summary—*p*-Dimethylaminophenylfluorone is investigated as a spectrophotometric reagent for germanium. In hydrochloric acid-ethanol solution a stable extinction is obtained over at least 20 hr without the use of a stabilising agent. The reaction is sensitive and Beer's law is followed up to concentrations of 0·24 μg of germanium/ml. Different factors able to influence the determination are investigated: reagent concentration, acidity, temperature and amount of water. Possible interference of the most common ions is examined, from which it appears that the proposed method is highly selective. The composition of the complex is finally determined by Job's continuous variation method. It can be shown that the germanium:fluorone ratio in the complex is 1:4.

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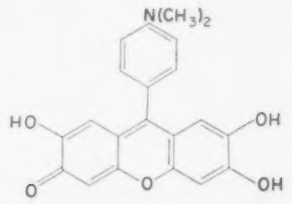
INTRODUCTION

HILLEBRANT and Hoste[1] proposed a spectrophotometric determination of germanium with phenylfluorone after benzyl alcohol extraction. In this way the use of a stabilising agent, which is necessary to prevent the precipitation of the insoluble complex in aqueous solution, is avoided. The determination is also feasible in methyl isobutyl ketone as was shown by Senise and Sant'Agostino.[2]

Another method to avoid difficulties arising from precipitation of the complex was suggested by Kimura *et al.*[3] who proposed a new fluorone derivative, dimethylaminophenylfluorone (I).



I

As this reagent contains a basic group, it was expected that a colloidal germanium complex would be avoided in an acidic aqueous medium. This was not substantiated by Kazarinova and Vasil'eva,[4] who found that the complex still showed colloidal character, although a stable extinction was claimed. The method proposed by these authors is, however, quite insensitive. Moreover, Beer's law is valid only for optical densities up to 0·16 so that germanium determinations are only possible over a very limited range. Our work, which was already in progress when we took cognisance of this research, does not confirm these results. It seemed worthwhile, therefore, to report our investigation, in which a sensitive, direct spectrophotometric determination of germanium is proposed, since extraction procedures are time consuming and not always desirable.

1

Although stable and reproducible results are obtained with phenylfluorone if gum arabic is used as a protective colloid,[5] the proposed method has the following advantages:

1. Beer's law is valid for germanium concentrations between 0·04 and 0·24 μg/ml.
2. Arsenic does not interfere, even in a 1000:1 ratio.
3. The sensitivity is about twice as high.

EXPERIMENTAL

Apparatus

Beckman DU or DK–1 spectrophotometer, 1·000-cm Corex cuvettes.

Reagents

Germanium stock solution: 1·4408 g of high purity germanium dioxide is dissolved in warm double-distilled water and made up to 1 litre in a calibrated flask.

Reagent solution, 0·05%: Prepared by dissolving 50 mg of fluorone in ethanol in the presence of 0·82 ml of 12·2*N* hydrochloric acid and diluting to 100 ml with ethanol.

TABLE I.—EXTINCTION AS A FUNCTION OF TIME IN AQUEOUS SOLUTION

HCl, *N*	Extinction at various times *hr*,						
	0·5	1	2	3	5	6	8
0·1	0·800	0·754	0·719	0·702	0·683	0·675	0·667
0·25	0·700	0·691	—	0·660	0·636	0·634	0·627
0·5	0·595	0·631	0·612	0·610	0·595	0·570	0·553
1	0·279	0·333	0·365	0·367	0·334	0·328	0·317
2	0·105	0·134	0·149	0·143	0·133	0·135	0·133

Stability of the complex in aqueous solution

As a basic group is present in the reagent, one would expect that an adequate acidity might solubilise the germanium complex. Hydrochloric acid was chosen, since germanium is usually separated by distillation or liquid-liquid extraction from this medium. The extinction of the germanium complex was examined as a function of time at hydrochloric acid concentrations of 0·1, 0·25, 0·5, 1 and 2*N*.

Four ml of germanium dioxide solution (5 μg of germanium/ml) were introduced into a 25-ml calibrated flask, 4 ml of reagent solution added and the solution made up to the mark with water and hydrochloric acid. The extinctions were measured versus germanium-free blanks at 504 mμ (wavelength of maximum extinction).

The reagent concentration used corresponds to a reagent:germanium molar ratio of 20:1. From Table I the extinction is seen to decrease with increasing acidity, as already found by Kazarinova and Vasil'eva.[4] A stable extinction was not, however, observed. A larger excess of reagent, namely at reagent: germanium ratios of 60:1, 80:1 and 100:1, does not improve the stability.

Stability of the complex in alcoholic solution

Because the germanium complex obviously still has colloidal properties in an aqueous medium, it was ascertained whether the use of ethanol would avoid the observed instability.

One ml of germanium dioxide solution (5 μg of germanium/ml) was introduced into a series of 25-ml calibrated flasks, then 3 ml of reagent solution followed by 0·18, 0·49, 1 and 2 ml of 12·2*N* hydrochloric acid were added. The solutions were diluted to the mark with ethanol, giving acid strengths of respectively 0·1, 0·25, 0·5 and 1*N*. The extinctions were measured versus blanks at 506 mμ (0·1 and 0·25*N* solutions) or at 513 mμ (0·5 and 1*N* solutions), corresponding to the wavelengths of maximum absorption.

TABLE II.—EXTINCTION AS A FUNCTION OF TIME IN ETHANOLIC SOLUTION

HCl, *N*	Extinction at various times *hr*,						
	0·5	1	2	3	6	8	20
0·1	0·375	0·385	0·389	0·387	0·382	0·383	0·392
0·25	0·362	0·366	0·361	0·361	0·357	0·358	0·360
0·5	0·380	0·387	0·376	0·367	0·367	—	0·375
1	0·203	0·206	0·206	0·197	0·205	—	0·207

From Table II it appears that the measured extinctions are considerably higher in an ethanolic medium than in water and are stable over at least 20 hr. It is also apparent that up to 0·5*N* hydrochloric acid, the sensitivity is nearly independent of the acid concentration. A concentration of 0·5*N* hydrochloric acid was chosen for further work, because the coloration of the blanks decreases with increasing acidity.

Influence of reagent concentration

In 0·5*N* hydrochloric acid the influence of the reagent concentration was examined as a function of time. Five reagent:germanium molar ratios were investigated, namely 20:1, 40:1, 60:1, 80:1 and 100:1. This showed that the maximum sensitivity is attained with a 60-fold excess. In this case a stable extinction is obtained after about 0·5 hr lasting for at least 20 hr.

Influence of the amount of water present

Because germanium is usually present in aqueous hydrochloric acid solution in actual analytical problems, the maximum admissible amount of water was investigated.

Five μg of germanium, dissolved respectively in 1, 2 and 5 ml of water, were introduced into 25-ml flasks. Three ml of reagent solution and 1 ml of 12·2*N* hydrochloric acid were added and the solutions made up to the mark. The extinctions were measured versus blanks at a wavelength of 513 mμ.

TABLE III.—INFLUENCE OF AMOUNT OF WATER PRESENT

Amount of water containing 5 μg of Ge, *ml*	Extinction at various times *hr*,						
	0·5	1	2	3	4	6	22
1	0·377	0·378	0·374	0·370	0·371	0·370	0·368
2	0·378	0·380	0·378	0·376	0·378	0·371	0·377
5	0·309	0·315	0·324	0·330	0·331	0·332	—

It appears from Table III that the maximum admissible amount of water is 2 ml for a 25-ml total solution. Higher water contents lower the sensitivity and give rise to less stable colorations.

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Influence of the order of mixing of the reagents

Although stable extinctions were obtained under the conditions outlined above, it appeared that the results were not reproducible in different series of experiments. It was shown that a definite order of addition of the reagents should be observed as well as certain standing periods. The final procedure, giving stable and reproducible results, is summarised below.

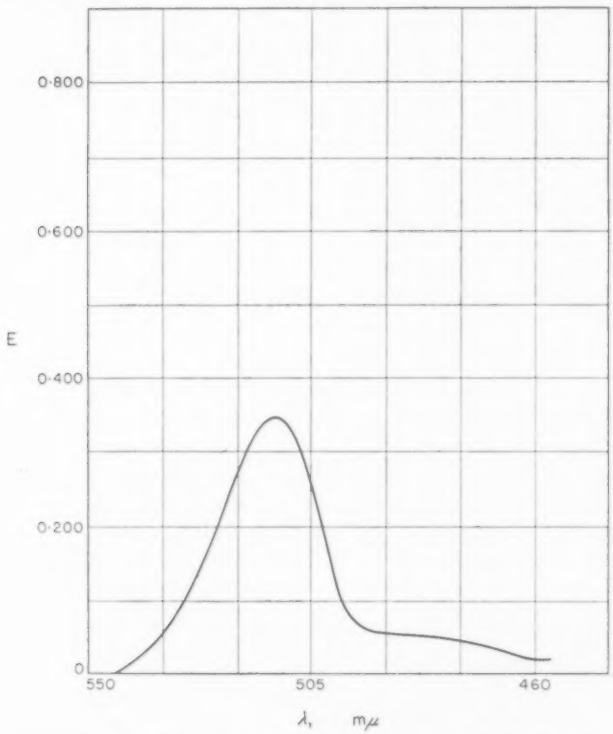

FIG. 1.—Absorption spectrum of the germanium complex

Two ml of the solution under investigation, 6*N* in hydrochloric acid, are introduced into a 25-ml calibrated flask. If the germanium is present as the dioxide instead of the tetrachloride, a standing period of 20 min is necessary after the addition of the required amount of concentrated hydrochloric acid before the next step is taken. Three ml of reagent solution are added. After 10 min the solution is made up to the mark with ethanol. The extinction is measured versus a blank at a wavelength of 513 mμ. This corresponds to the wavelength of maximum absorption (see Fig. 1 for the absorption curve, registered by means of a Beckman DK–1 spectrophotometer).

Influence of temperature

Kazarinova and Vasil'eva[4] had already found that the extinction is strongly dependent on the temperature. This temperature dependency was examined systematically and the results are summarised in Fig. 2.

As is apparent from Fig. 2, the extinction appears to be a linear function of temperature from 19° to 27° and can be represented by the following equation, where 20° is taken as reference:

$$E_{t°} = E_{20°} + 0{\cdot}0317\,(20 - t°).$$

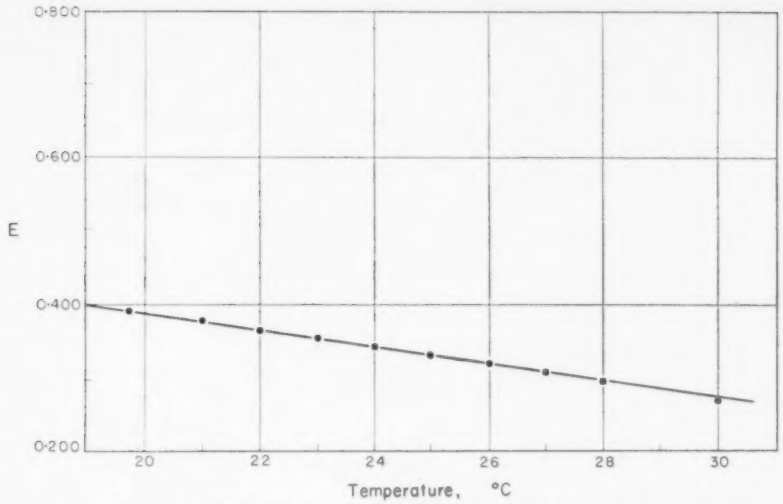

FIG. 2.—Extinction of the germanium complex as a function of temperature.

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Calibration curve

To examine the adherence to the Lambert–Beer law, the extinction was measured as a function of the germanium concentration at a temperature of 19°. The results are represented in Table IV.

TABLE IV.—CALIBRATION CURVE

μg of Ge/*ml*	E	$\bar{k} = \frac{E}{c}$	$\overline{\Delta k}$
0·04	0·080	2·00	0·005
0·06	0·120	2·00	0·005
0·08	0·159	1·99	0·005
0·10	0·201	2·01	0·015
0·12	0·242	2·016	0·021
0·14	0·279	1·99	0·005
0·16	0·318	1·987	0·008
0·18	0·358	1·99	0·005
0·20	0·398	1·99	0·005
0·22	0·438	1·99	0·005
0·24	0·476	1·983	0·012
0·28	0·545	1·95	0·045
0·32	0·612	1·912	0·083
0·36	0·676	1·88	0·115
0·40	0·732	1·83	0·165

It appears that Beer's law is valid up to 0·24 μg of germanium/ml: extinction coefficient, $\bar{k} = \frac{E}{c} = 1{,}995$ (c in μg/ml); standard error (for 0·04 up to 0·24 μg of germanium/ml), $\sqrt{\frac{\sum \bar{\Delta}k^2}{10}} = 0{\cdot}010$ or 0·50%; molar extinction coefficient, $\bar{\varepsilon} = 1{\cdot}995 \times 1000 \times 72{\cdot}6 = 1{\cdot}45 \times 10^5$.

Influence of foreign ions

The influence of foreign ions, up to a ratio of 1000:1 of foreign ion:germanium was investigated. The cations were present as their chlorides, the anions as their sodium, potassium or ammonium salts. The results are presented in Table V.

TABLE V.—INFLUENCE OF FOREIGN ION

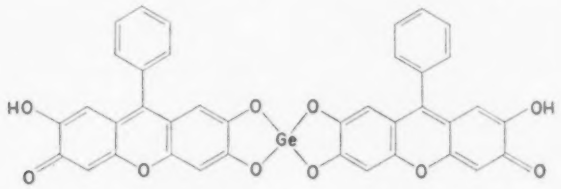
Foreign ion	Extinction for various ratios of foreign ion:germaniun			
	1:1	10:1	100:1	1000:1
As^{III}	—	0·384	0·382	0·383
Sb^{III}	0·383	0·417	0·711	—
Sn^{II}	0·385	0·448	1·680	—
Mo^{VI}	0·424	0·650	—	—
Bi^{III}	—	0·390	0·401	—
Fe^{III}	—	0·388	0·389	0·440
Ti^{IV}	0·387	0·475	1·440	—
Ga	0·388	0·396	0·403	—
Na	—	—	0·390	0·389
K	—	—	0·390	0·391
Li	—	—	0·387	0·386
Mg	—	—	0·386	0·395
Ba	—	—	0·386	0·395
Ca	—	—	0·385	0·384
Cu^{II}	—	—	0·397	0·528
Co^{II}	—	—	0·385	0·410
Ni^{II}	—	—	0·388	0·393
Mn^{II}	—	—	0·389	0·387
Zn^{II}	—	—	0·386	0·383
Hg^{II}	—	—	0·390	0·416
Cd^{II}	—	—	0·388	0·387
Al^{III}	—	—	0·386	0·447
Cr^{VI}	—	0·398	0·444	0·935
Zr^{IV}	0·457	0·765	2·230	—
Br^-	—	—	0·391	0·388
F^-	—	—	0·387	0·385
SO_4^{2-}	—	—	0·384	0·387
SO_3^{2-}	—	—	0·383	0·384
NO_3^-	—	—	0·388	0·386
$H_2PO_4^-$	—	—	0·382	0·384
Ox^{2-}	—	—	0·387	0·275
Tartrate	—	—	0·393	0·376
Citrate	—	—	0·388	0·373
TeO_3^{2-}	—	—	0·389	0·370
Biphthalate	—	—	0·384	0·376

It appears that As^{III}, Na, K, Li, Mg, Ba, Ca, Ni, Mn^{II}, Zn, Cd, Br^-, F^-, SO_4^{2-}, SO_3^{2-}, NO_3^- and $H_2PO_4^-$ in a 1000:1 proportion do not interfere.

Fe^{III}, Cu^{II}, Hg^{II}, Al, Ox^{2-}, tartrate, citrate, TeO_3^{2-} and biphthalate are admissible in a 100:1 proportion, whereas Bi^{III}, Ga and Cr^{III} should be limited to a 10:1 ratio. The Sb^{III}, Sn^{II} and Ti^{IV} to germanium ratio should not exceed 1:1, whereas Mo^{VI} and Zr^{IV} should be absent.

Composition of the complex

Stipanits and Hecht[6] have already demonstrated that the germanium–phenylfluorone complex, isolated from an aqueous solution, corresponds to the formula



II

To determine the composition of the *p*-dimethylaminophenylfluorone complex in alcoholic solution, Job's continuous variation method[7] was used. The results, giving the measured extinctions as a function of the [germanium]:[germanium + reagent] ratios at a wavelength of 513 mμ are presented in Fig. 3.

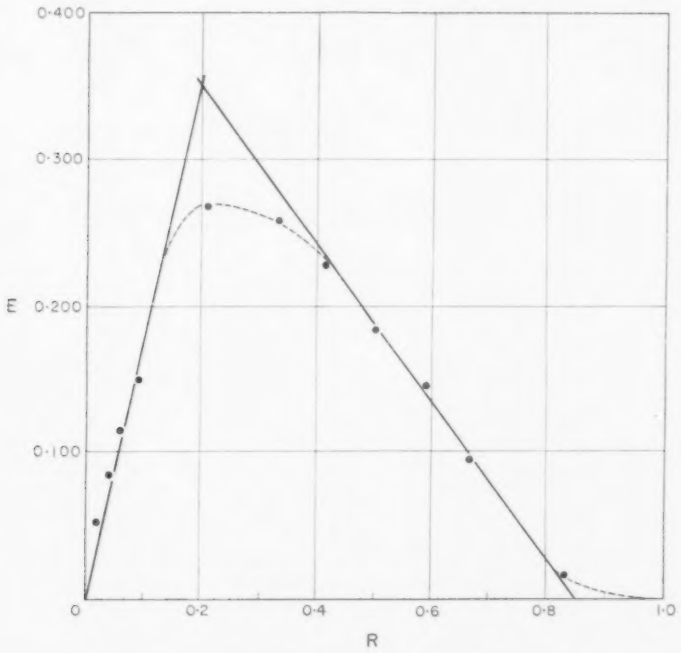


FIG. 3.—Extinction as a function of [Ge]/[Ge + reagent] ratio.

From Fig. 3 it is apparent that the extrapolated maximum extinction occurs at a [Ge]/[Ge + reagent] value of 0·197. This value is in close agreement with a germanium:reagent ratio of 1:4.

Zusammenfassung—*p*-Dimethylaminophenylfluoron wurde im Hinblick auf seine Verwendung als photometrisches Reagens für Germanium untersucht. Unter Anwendung eines Stabilisators konnte in einer Salzsäure-Alkohol-Mischung eine über wenigstens 20 Stunden stabile Färbung erzielt werden. Die Reaktion ist empfindlich und Beers Gesetz wird hinauf bis zu Mengen von 0·24 μg Ge/ml erfüllt.

Verschiedene Faktoren, die die Bestimmung beeinflussen wurden untersucht. Konzentration des Reagenses, Säuregehalt, Temperatur und Wassergehalt wurden daraufhin studiert. Studien über den Einfluss der gewöhnlichen Metalle führten zum Schluss, dass die Methode hohe Selektivität aufweist. Die Zusammensetzung des Komplexes wurde nach der Job-Methode ermittelt und das Verhältnis Ge:Reagens als 1:4 festgestellt.

Résumé—La *p*-diméthylaminophénylfluorone a été étudiée comme réactif spectrophotométrique du germanium. En solution acide chlorhydrique éthanol une extinction stable est obtenue pendant au moins 20 heures sans utiliser d'agent stabilisant. La réaction est sensible; la loi de Beer est suivie jusqu'à des concentrations de 0,24 μg Ge/ml. Différents facteurs pouvant influencer le dosage ont été étudiés: concentration du réactif, acidité, température et teneur en eau. L'interférence possible de la plupart des ions a été examinée: il s'ensuit que la méthode proposée est très sélective. La composition du complexe a été déterminée par la méthode des variations continues de Job, et le rapport germanium/fluorone trouvé égal à 1/4.

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DETERMINATION OF WATER BY NEAR-INFRARED SPECTROPHOTOMETRY

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Summary—Water may be determined in methanol, isopropanol, dioxan, glycols and polyols using near-infrared spectrophotometric methods. Polar solvents have their maximum absorbance for water at longer wavelengths than non-polar solvents, and the non-polar solvents have larger extinction coefficients than polar solvents.

A screen reference has been substituted for the dry solvent reference in one method for the determination of water in methanol and in isopropanol. In this method reproducible settings of the screen attenuator and other instrument variables have been accomplished by a chloroform reference.

A base line technique employing a screen attenuator instead of a dry solvent reference has been developed to determine small amounts of water in polyols.

A differential spectrophotometric method employing ethylene glycol of known water content has been designed for measuring water in anti-freeze mixtures. This near-infrared method has the advantages of being non-destructive and rapid. Results compare favourably with values from Karl Fischer titrations and gas chromatography.

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INTRODUCTION

THE presence of water bands in the near-infrared region has been the subject of many studies.[1,2] Recently, in an excellent review of near-infrared spectroscopy Kaye[3] has suggested that water should be one of several substances determinable by near-infrared spectrophotometry. Despite this suggestion, relatively few analytical methods have appeared,[4–6] probably largely due to the difficulty of obtaining suitable apparatus for the determination. With the present development and availability of reliable spectrophotometers for this spectral region, the near-infrared determination of water should become more commonplace.

Although difficulties may be encountered in the use of the near-infrared region for water determination, a variety of techniques are available which render the near-infrared method for water versatile, accurate and rapid. Several examples of near-infrared methods for the determination of water in a variety of samples are included to demonstrate the techniques used and the results which may be expected.

EXPERIMENTAL

The Perkin Elmer Model 4000 Spectrophotometer was used for these studies. The water absorption at 1·9 μ was used in preference to that at 1·4 μ or other wavelengths because of the greater absorbance of water at 1·9 μ. No special thermostatting was employed since the data show that it is unnecessary, and previous authors[6] have already studied temperature effects and found them to be minor.

Solvent evaporation was reduced by appropriate precautions, and hygroscopic samples were protected wherever the data showed the necessity of such precautions.

RESULTS AND DISCUSSION

Differential methods

Differential methods employing a reference of known water concentration and composition, nearly identical to the sample except for water content, were used. These methods were shown to be able to detect the water difference between the water contained in the sample and the reference with good precision.

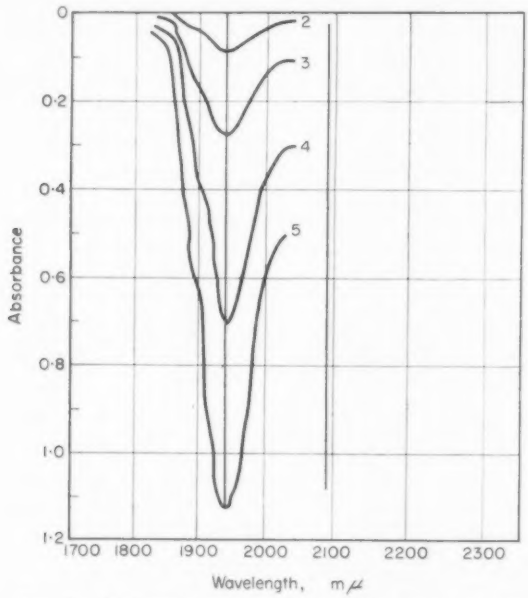

FIG. 1.—Constancy of λ_{max} for increasing water in methanol.
Water content: 1, 0·0%; 2, 0·2%; 3, 0·6%; 4, 1·50%; 5, 2·45%.

TABLE I—WATER DETERMINATION IN METHANOL—COMPARISON OF NIR AND KARL FISCHER METHODS

%H_2O added	%H_2O by NIR	% H_2O by KF	Error (NIR)	Error (KF)
0·03	0·00	0·03	−0·03	0·00
0·10	0·10	0·14	0·00	+0·04
0·30	0·30	0·37	0·00	+0·07
1·00	1·00	1·03	0·00	+0·03
2·00	2·09	2·06	+0·09	+0·06
3·00	3·05	2·91	+0·05	−0·08
4·00	3·88	3·97	−0·12	−0·03

The differential method was studied for a variety of systems. One of the simplest was the methanol-water system (Fig. 1). A water content as low as 0·1 and up to 2·5% may be determined (Table I) using 1-cm cells. A dry methanol reference is used. No difficulties such as shifts in the wavelength of maximum absorbance were observed (Fig. 1). Fig. 2 shows that the absorbance at 1·94 μ is proportional to concentration for this water range. Methanol samples containing more than 2% of water can be analysed after mixing with known weights of dry methanol to reduce the water content

of the new sample to the optimum range. In such a fashion, water contents exceeding 50% were measured without any further difficulties (Table II). Methanol need not be dry to serve as a reference, but the water concentration in the methanol must be known. Water content differences which are measured by near-infrared spectrophotometry differentially can then be easily corrected to a dry reference basis. The

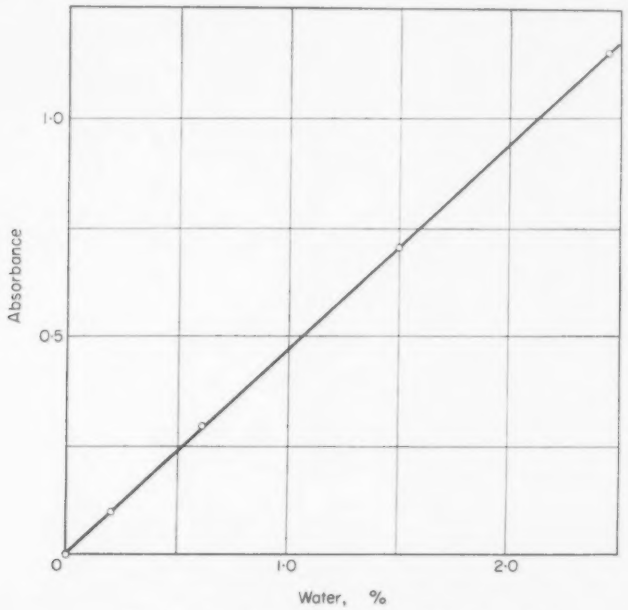

FIG. 2.—Absorbance of water in methanol at 1·94 μ.

TABLE II—ANALYSIS OF HIGH WATER-CONTENT METHANOL

Wt. % H_2O added	Sample wt., *g*	Wt. after dilution, *g*	Absorbance	Wt. H_2O* % found
5·0	10	100	0·23	4·9
15·0	15	100	1·06	15·0
30·0	5	100	0·72	30·5
60·0	5	100	1·43	61·0

* Wt. % H_2O found $= \dfrac{\text{(Absorbance)(Dilution wt.)}}{\text{(0·47)(Sample wt.)}}$

where 0·47 is the proportionality constant in the equation.

Absorbance = (0·47) (1 cm) (Wt. % H_2O in methanol).

concentration of water in a reservoir of methanol can be determined by Karl Fischer analysis. Thereafter, water contents can be determined by near-infrared, using this reference, much more rapidly than by further Karl Fischer titrations, because of the elimination of sample weighings and of the titration itself. Filling a sample cell and scanning the 1·94 μ region of the near-infrared requires only a few min. For routine samples, therefore, the differential method is very time saving over conventional, non-spectrophotometric methods. This differential method has been used to determine water in isopropanol, ethanol, dioxan and ethylene glycol.

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Five different ethylene glycol-type commercial antifreezes were examined for their water content using an ethylene glycol of known water content (determined by Karl Fischer titration) as the reference. No difficulties were apparent, despite the fact that some of these anti-freeze mixtures contained inorganic tetraborates, sodium 2-mercaptobenzothiazole, arsenites, nitrites and other additives (Fig. 3). Results from

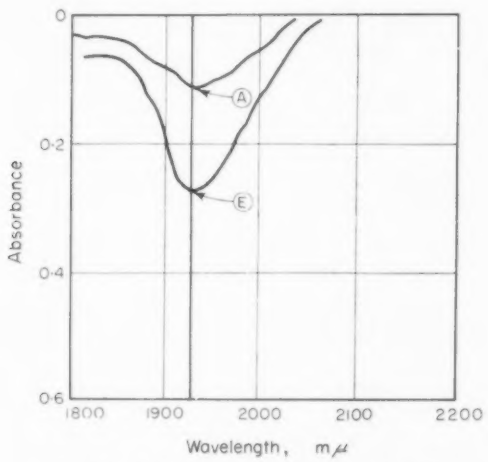

FIG. 3.—Absorbance of water in antifreezes.
Water content: Sample A, 2·20%; Sample E, 4·51%; Ethylene glycol reference, 1·41%.

the ASTM method D1123, a proposed revision of *Water in Concentrated Engine Antifreezes by the Iodine Reagent Method*, which minimises undesirable interfering reactions caused by the antifreeze additives,[7] and a chromatographic method, are compared with the near-infrared method (Table III). Results for the chromatographic

TABLE III—DETERMINATION OF WATER IN ANTIFREEZE

Sample	Water, %		
	ASTM	NIR	GLC
A	2·2	2·3	2·1
B	3·4	3·5	3·3
C	3·2	3·1	3·1
D	5·0	4·9	4·9
E	4·1	4·5	4·2

method employing Fluoropak 80 substrate solid (from the Fluorocarbon Co., Fullerton, Calif.) and the partition liquid, polyethylene glycol 400 (Carbide and Carbon Chemicals Corp., New York 17, N.Y.) are shown in Fig. 4. A comparison of the results shows good agreement between the three methods, but the near-infrared method was by far the most rapid.

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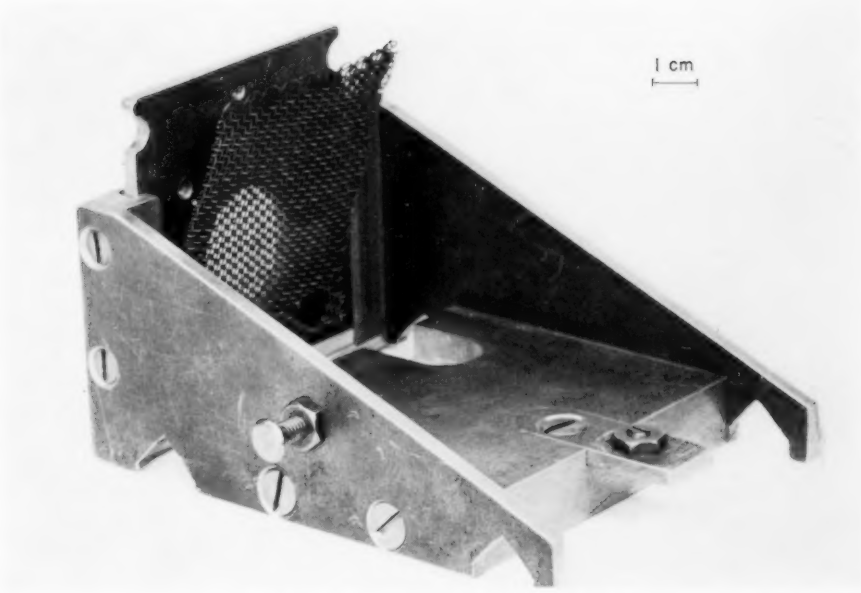

FIG. 5.—Screen attenuator for reference cell.

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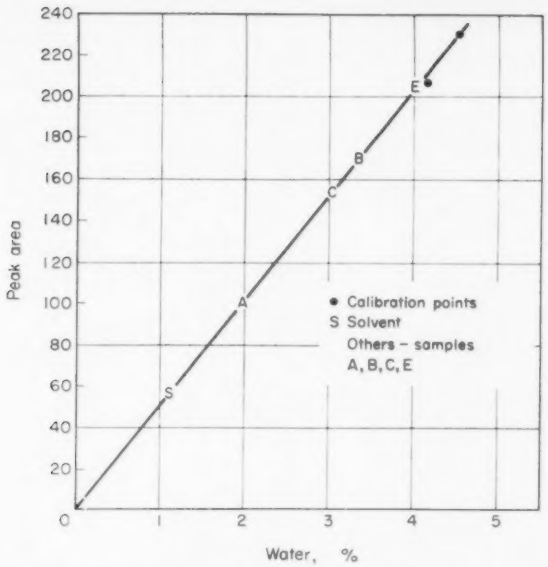

FIG. 4.—Chromatographic (GLC) method for water in antifreeze.

Screen attenuation

The differential spectrophotometric approach requires suitable references of known water content, which are often difficult to obtain. If a screen attenuator (Fig. 5) is substituted for the reference solvent, many samples will show absorbances in the 1·9-μ region which can be related by a base-line technique to water content. The screen attenuator is used to adjust the light energy of the reference beam so that the pen tracing of the instrument falls within the range of the recorder chart. The absorbance of the regions adjacent to the 1·9-μ peak are recorded. A base line is drawn which estimates the absorbance from structures other than water, and thereby permits the estimation, by difference from total absorbance, of that absorbance due to water. The screen attenuator should be able to reduce the light in a variable manner, and, once in place, should attenuate without change until moved to a new setting. The measurement of water in polypropylene glycol 2000 in the region of 0·01 to 0·15% illustrated a difficulty using this approach. The base-line absorbance (Fig. 6) was proportional to the water content in the desired region as shown by standard addition (Table IV). However, when the samples were dried by vacuum

TABLE IV—WATER IN POLYPROPYLENE GLYCOL 2000 BY BASE LINE SCREEN ATTENUATION NIR

% H_2O added	% H_2O found	% H_2O increase
0·00	0·124*	—
0·036	0·164	0·040
0·087	0·215	0·091
0·100	0·224	0·100
0·127	0·265	0·141

* Initial sample water by Karl Fischer was 0·008%.

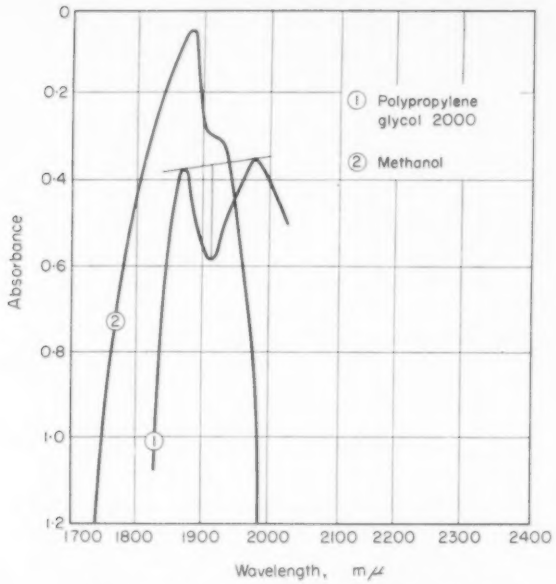

FIG. 6.—Base-line absorbance of water in alcohols.

distillation or with phosphorus pentoxide, a Karl Fischer titration showed complete water removal. The near-infrared method showed 0·11% water remaining. This apparent amount of water remaining was constant for several samples of polypropylene glycol 2000 which were carefully dried. This suggested that the difference was due to a small constant peak absorbance at 1·9 μ associated with the polypropylene glycol 2000 structure. When the 0·11% "correction" is subtracted from the value obtained by the screen attenuation base-line technique, the near-infrared and Karl Fischer methods are in agreement.

An instrument reference

Attempts to eliminate the need of a reference methanol standard, using a screen attenuation base-line approach, failed because methanol has a peak adjacent to the 1·9-μ peak (Fig. 6) which causes interference. However, when a series of synthetic methanol-water mixtures were prepared by the addition of water to dry methanol the increase in absorbance at 1·94 μ was proportional to the water content increase.

To use the chloroform instrument reference, the spectrophotometer and the screen attenuator in the reference beam were adjusted to give 0% transmittance for no light (closed shutter), and 100% transmittance at 1·94 μ for a dry methanol solution. When the methanol was replaced by chloroform, the absorbance at 1·69 μ was measured and found (Fig. 7) to be 1·2 absorbance units (A). To produce equivalent settings on another day, without recourse to dry methanol, the chloroform solution could be used to adjust the instrument to read 1·2 A. at 1·69 μ. Thereafter, the absorbance at 1·94 μ in the methanol samples was directly proportional to the water content of the methanol. Therefore this determination no longer requires dry solvents, or solvents of known water content. The chloroform peak, which is due to main structural features of chloroform, is not sensitive to small changes of impurities in the

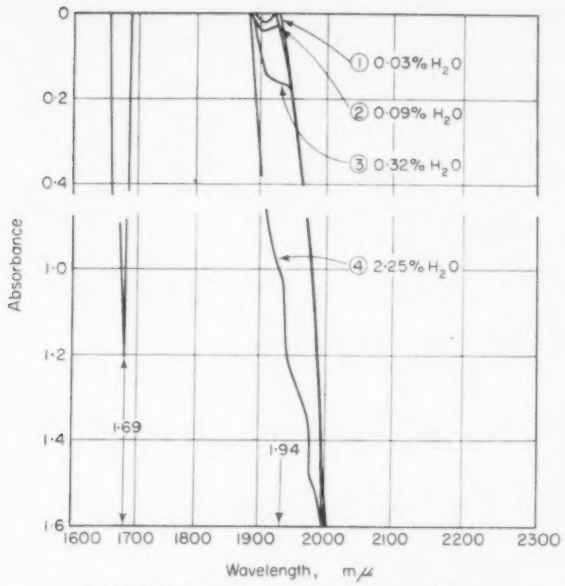

FIG. 7.—Setting screen attenuator using chloroform.

chloroform, and need not be protected from water, as is necessary with a dry methanol reference. This technique was used with success to reproduce instrument settings, on several different days, by several operators (Table V).

TABLE V—DETERMINATION OF WATER IN METHANOL USING A CHLOROFORM REFERENCE

% H_2O added	% H_2O by KF	% H_2O by NIR	
		1st day	2nd day
0·03	0·03	0·01	0·01
0·13	0·14	0·11	0·09
0·33	0·37	0·30	0·34
1·02	1·03	1·00	1·00
1·99	2·06	2·07	2·06
2·95	2·91	3·11	3·04
3·87	3·97	3·82	3·76

Position and intensity of absorbance

Of the solvents studied, the strongly polar solvents have their maximum absorbance for water at longer wavelengths than the non-polar solvents (Fig. 8), and the non-polar solvents have larger proportionality constants than the polar solvents (Table VI). For any new system the wavelength of maximum absorbance should be determined by adding a small amount of water to the sample and using the drier sample as a reference for a differential scan through the 1·9-μ region. The proportionality constant between the water content in the sample being studied and the absorbance may be determined at the same time if a known weight of water is added to a known weight of sample.

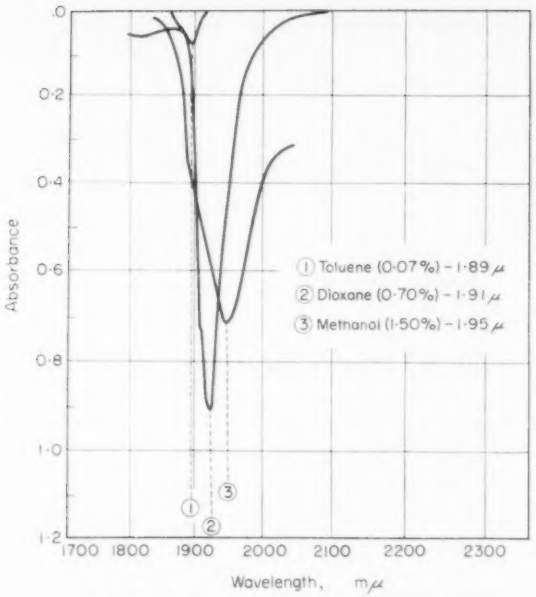

FIG. 8.—Dependence of λ_{max} on solvent polarity.

TABLE VI—WAVELENGTH OF MAXIMUM ABSORBANCE AND PROPORTIONALITY CONSTANTS FOR WATER IN DIFFERENT SOLVENTS

Solvent	λMax., μ	ε(Wt. %)*	εm†
Toluene	1·89	1·04	1·6
Methanol	0·94	0·47	0·68
Isopropanol	1·94	0·50	0·71
Dioxan	1·91	1·29	2·46
Polypropylene glycol 2000	1·91	1·03	1·89
Ethylene glycol	1·96	0·227	0·46

$$* \varepsilon \text{ wt. } \% = \frac{\text{(Absorbance)}}{\text{(1 cm)(wt. \% } H_2O\text{)}}$$

$$\dagger \varepsilon m = \frac{\text{(Absorbance)}}{\text{(1 cm)(Moles of water per 1000 ml of solution)}}$$

Water in solids and emulsions

Water in solids and emulsions, such as liquid soaps, may often be measured by dissolving the material in methanol or some other suitable solvent, and measuring the increase in absorbance at the 1·9-μ peak. Some success has been achieved with leaching water from finely ground insoluble "solids," although it should be recognised that some samples contain substances which obscure the 1·9 μ region, and some samples fail to give up their water to the solvent.

CONCLUSION

The above experimental observations show that near-infrared spectrophotometry is able to measure water in a variety of systems. Near-infrared methods possess the advantages of being non-destructive, rapid and accurate.

Zusammenfassung—Wasser kann durch spectrophotometrische Messung im nahen IR-Bereich bestimmt werden in: Methanol, Isopropanol, Dioxan, Glykolen und Polyolen. Polare Lösemittel haben das Absorptionsmaximum für Wasser bei längeren Wellenlängen als nonpolare. In nonpolaren Lösemitteln ist der Extinktionskoeffizient grösser als in polaren. Bei der Bestimmung von Wasser in Methanol und Isopropanol wurde an Stelle des trockenen Lösemittels eine Blende als "Blindlösung" verwendet. Eine "Grundlinien-Technik" wurde herangezogen unter Verwendung einer Blende an Stelle des getrockneten Lösemittels, wenn kleine Wassergehalte in Polyolen zu bestimmen waren. Eine differentielle spectrophotometrische Methode wurde herangezogen um Wasser in Frostschutzmitteln zu bestimmen. Die neue Methode hat den Vorteil schnell zu sein und die Probe nicht zu zerstören. Resultate sind in guter Übereinstimmung mit denen nach der Karl-Fischer-Methode und gaschromatographischen Ergebnissen.

Résumé—L'eau peut être dosée dans le méthanol, l'isopropanol, le dioxanne, les glycols et les polyols par des méthodes spectrophotométriques dans le proche infrarouge. Le maximum d'absorption pour l'eau des solvants polaires se trouve à des longueurs d'ondes plus élevées que pour les solvants non polaires; les solvants non polaires ont des coefficients d'absorption plus grands que les solvants polaires. Une référence constituée par un écran a été substituée au solvant sec dans une méthode de dosage de l'eau dans le méthanol et l'isopropanol. Dans cette méthode, des montages reproductibles de l'écran atténuateur des autres variables instrumentales ont été accomplis à l'aide d'une référence au chloroforme. Une technique de base utilisant un écran atténuateur à la place du solvant sec comme référence a été mise au point pour doser de faibles quantités d'eau dans les polyols. Une méthode spectrophotométrique différentielle employant de l'éthylène glycol dont la teneur en eau est connue a été conçue pour mesurer la quantité d'eau dans les mélanges anti-gel. Cette méthode dans le proche infra-rouge présente les avantages d'être non destructive et rapide. Les résultats se comparent de manière favorable aux valeurs obtenues par les titrages Karl Fischer et la chromatographie des gaz.

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THE DETERMINATION OF THIOMALIC ACID*

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Summary—A method has been developed for the determination of thiomalic (mercaptosuccinic) acid based on its oxidation with an excess of iodine in a strongly alkaline medium and back-titration of the latter with thiosulphate solution after acidification. Thiomalic acid may also be titrated as a dibasic acid using a glass electrode.

IN connection with the study of the reaction between quinque-or sexavalent molybdenum and thiomalic (mercaptosuccinic) acid, $HOOC{\cdot}CH_2CHSH{\cdot}COOH$,[1] it was necessary to have as rapid and simple a method for its determination in solution as possible. Apart from this, thiomalic acid is acquiring practical importance in medicine.

Recently a method has been proposed for the determination of thioalcohols and thiophenols[2] based on the addition to a weighed sample of the substance of an excess of a solution of acrylonitrile ($CH_2{=}CH{\cdot}CN$) in dioxan and determination of the excess of the acrylonitrile by the sulphite method. The method gives accurate results (error 0·3%) and it is applicable both to dry preparations and to aqueous solutions of thiomalic acid.

The present paper describes a method of establishing the concentration of thiomalic acid in aqueous solutions based on its oxidation with an excess of iodine in a strongly alkaline medium. In order to check the results obtained, the thiomalic acid was titrated with a solution of caustic soda, using a glass electrode (Fig. 1).

In contrast to many other compounds, the molecule of which contains a sulphydryl group, the reaction between thiomalic acid and iodine in an acid or weakly alkaline medium does not proceed stoichiometrically, either in the direct titration with iodine solution, or on the addition of an excess of iodine followed by titration with thiosulphate solution. In the first case, no definite and reproducible results were obtained; in the second, for 1 mole of thiomalic acid 1·84, 1·89 and 1·73 gram-equivalents of iodine (in 0·1*N* HCl) were consumed in three separate titrations.

Satisfactory results were obtained by oxidising thiomalic acid with iodine in a strongly alkaline medium under conditions similar to those used in the oxidation of dialkyl- and diarylthiophosphoric acids.[3]

To a predetermined volume of a standard solution of thiomalic acid, prepared from an accurately weighed sample of a pure analysed preparation, is added a 6N alkali solution and then an excess of standardised iodine solution; the quantity of alkali taken is calculated so that its concentration, after the addition of the iodine solution, falls within the range from 0·3*N* to 3*N*. The solution is allowed to stand for some time, sufficient sulphuric acid is added to produce a definite acid reaction with universal indicator paper, and the excess of iodine is titrated with thiosulphate solution. Under these conditions, 1 mole of thiomalic acid reacts, on the average, with 5·98 gram-equivalents of iodine (Table I).

* Translated from *Vestnik Moscowskogo Universiteta, Ser. khimii*, 470 1960, No. 4, 52.

Variations in the concentration of alkali within the range 0·3*N*–3*N* and in the time of standing, have practically no effect on the completeness of oxidation of the thiomalic acid.

Experiments show that aqueous solutions of thiomalic acid can be titrated with alkali solutions. The dissociation constant of thiomalic acid is $5{\cdot}23 \times 10^{-4}$ at 25°.[4]

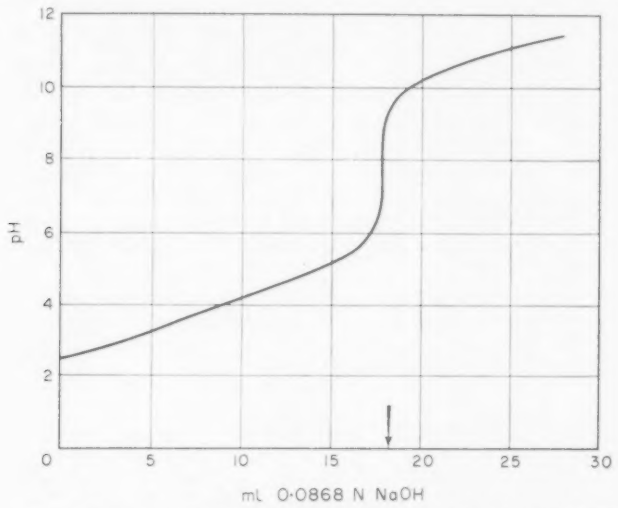

FIG. 1.—Potentiometric titration curve for thiomalic acid with NaOH
→—theoretical equivalence point

TABLE I. MOLAR RATIO BETWEEN THIOMALIC ACID AND IODINE ON REACTION IN A STRONGLY ALKALINE MEDIUM

Final concentration of NaOH, *N*	Time of standing for oxidation, *min*	Weight of thiomalic acid,* *mg*	Consumption of iodine in the oxidation, *mg*	Thiomalic acid found, *mg*†	Error *mg*	$M_{\text{thiomalic acid}} / M_{\text{iodine}}$
0·36	5	11·10	0·2239	11·20	+0·10	6·06
1·0	30	11·10	0·2316	11·60	+0·50	6·26
1·0	100	15·02	0·2845	14·24	−0·78	5·70
2·0	30	11·10	0·2100	10·81	−0·29	5·84
3·0	30	11·10	0·2230	11·16	+0·06	6·02

Mean: 5·98

* In the preparation used, 21·92, 22·19 and 22·08 % of HS was found by the method of Obtemperanskaya, Terent'ev and Buzlanova,[2] the theoretical content of HS being 22·05 %. The determinations were carried out by M. M. Buzlanova, to whom the authors express their thanks.

† On the assumption that 1 mole of thiomalic acid consumes 6 g-equiv of iodine.

The titration curve of 50 ml of $1{\cdot}6 \cdot 10^{-2}M$ thiomalic acid with caustic soda (0·08680*N*), using a glass electrode, is shown in Fig. 1.

A distinct break is observed at pH 5·5–9·5; thiomalic acid titrates as a dibasic acid (Table II). The concentration of thiomalic acid in solutions may probably, therefore, be determined by neutralisation in the presence of suitable indicators with a colour change at pH 6–9 (neutral red, phenol red, *etc.*).

Table II. Titration of thiomalic acid with alkali using a glass electrode

Weight of thiomalic acid, *g*	Consumption of NaOH solution (0·08680*N*), *ml*	Thiomalic acid found, *g*	Error, *g*	$\frac{M_{NaOH}}{M_{thiomalic\ acid}}$
0·1024	15·50	0·1010	−0·0014	1·975
0·0997	15·00	0·09778	−0·0019	1·961
0·1202	17·95	0·1170	−0·0032	1·961

Mean: 1·966

Zusammenfassung—Eine Methode zur Bestimmung von Thioäpfelsäure wurde entwickelt. Die Methode beruht auf der Oxydation der Säure mit überschüssigem Jod in stark alkalischem Medium und Rücktitration des unverbrauchten Jods nach Ansäuern der Lösung durch Thiosulfat. Es ist möglich die Thioäpfelsäure als zweibasische Säure an der Glaselektrode zu titrieren.

Résumé—Les auteurs ont mis au point une méthode de dosage de l'acide thiomalique; cette méthode est basée sur l'oxydation de l'acide par un excès d'iode en milieu fortement alcalin, suivie du titrage en retour de la solution obtenue par le thiosulfate après acidification. Il est possible de doser l'acide thiomalique avec une électrode de verre.

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SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN LOW-GRADE MINERALS AND ORES

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Summary—The following method is intended for the determination of microgram quantities of thorium in samples of minerals and ores. The mineral sample is decomposed by repeated sintering with sodium peroxide. After digestion of the product with water, thorium peroxide hydrate is recovered by centrifugation and dissolved in hydrochloric acid. Thorium is determined spectrophotometrically with naphtharson (the sodium salt of 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid) after its separation from metals forming chloro-complexes, which are adsorbed on a strongly basic anion-exchange resin. Interferences from a few different ions have been studied. The time required for the analysis of one sample is about 4 hr, when analysing 12 samples simultaneously.

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INTRODUCTION

THE sodium salt of naphtharson, 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid, has, during the last ten years, been used as a reagent in the spectrophotometric determination of thorium by several authors: Thomason, Perry and Byerly,[1] Banks and Byrd,[2] Grimaldi and Fletcher,[3] Clinch,[4] Fletcher, Grimaldi and Jenkins[5] and Everest and Martin.[6]

The low thorium content for which the method described in the present paper is intended makes it necessary to separate the thorium from many other elements, in order to avoid interferences in the spectrophotometric determination. Grimaldi, Jenkins and Fletcher[7] have accomplished a separation by precipitating thorium selectively as iodate from a solution containing tartaric acid and hydrogen peroxide.

Kraus, Moore, Nelson and Smith have, during the years 1950–1956, published a number of papers dealing with the adsorption, on the strongly basic anion-exchange resin, Dowex 1, of different metals having the ability to form chloro-complexes. From these investigations, it is clear that thorium does not form chloro-complexes which can be adsorbed.[8] For this reason, it may be expected that in concentrated hydrochloric acid a good separation of thorium from several metals can be obtained by the use of a strongly basic anion-exchange resin.

During the early stages of the work described here, it was found that this is indeed the case. Meanwhile, Nietzel, Wessling and De Sesa published a method for the determination of thorium, where a separation of thorium based on the same principle is used.[9]

REAGENTS AND APPARATUS

All reagents used were of analytical grade.
Sodium peroxide: Mallinckrodt Calorimetric Powder analytical reagent.
Sodium hydroxide: 1% solution free from carbonate.
Hydrochloric acid: Conc. and 1:3.
Hydrogen peroxide: Fresh solution of Perhydrol (Merck.) 1:10.

Ammonia: A fresh, nearly saturated solution obtained by dissolving gaseous ammonia in CO_2-free distilled water under cooling.

Aluminium chloride: Aqueous solution containing 1 mg of Al/ml.

Ascorbic acid: 2·5 g in 50 ml of distilled water. This is freshly prepared for use.

Naphtharson:* 1 g of 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid in 1 litre of distilled water. For the present investigation, naphtharson with the trade name *Thoron* (Fine Organics Inc., 205 Main Street, Lodi, N.J., U.S.A.) was used. A calibration curve is prepared for each new solution of the reagent.

Ion-exchange resin: Dowex 1–X 10, 50–100 mesh, for analytical purposes.

Ion-exchange column: The ion-exchange resin is contained in a glass tube 1 cm in diameter and 15 cm in length. The tube is somewhat tapered at its lower end. On its upper end a wider tube, with a diameter of 2·5 cm and a length of 10 cm, is attached. A piece of glass wool is placed in the tapered end of the 1-cm tube. Above the glass wool the tube is filled with the ion-exchange resin up to the wider tube, and on top of the resin another piece of glass wool is placed. The ion-exchange resin, if obtained in carbonate form, should be converted to the chloride form before being transferred to the glass tube.

Centrifuge: A laboratory centrifuge with 6 tubes of 50-ml capacity.

Spectrophotometer: A Beckman spectrophotometer Model B with 5-cm glass cells was used.

PROCEDURE

1. Weigh about 100 mg of the finely ground mineral in a small platinum crucible and add 2 g of sodium peroxide. Mix thoroughly with a small platinum rod.
2. Sinter the mixture for 45 min in an electric furnace at 430° ± 10°.
3. Digest the content of the crucible with 150 ml of cold water, heat the solution to boiling, and filter through a retentive filter paper.
4. Wash with 1% sodium hydroxide, place the filter in the platinum crucible, and ignite.
5. Sinter the residue in the crucible with 1 g sodium peroxide for 30 min at 430° ± 10°.
6. Repeat operations 3–5 once and proceed thereafter according to 7.
7. Transfer the sintered mass to a 50-ml centrifuge tube. Add distilled water. Rinse the crucible with distilled water into the centrifuge tube, and digest the suspension.
8. Centrifuge, and remove the supernatant liquid with the aid of a pipette connected to a water suction pump.
9. Dissolve the precipitate in 5 ml of hydrochloric acid (1:3) and dilute with 35 ml of hot CO_2-free distilled water.
10. Add 5 ml of 3% hydrogen peroxide and an excess of freshly prepared ammonia solution.
11. Centrifuge and wash the precipitate with warm dilute ammonia (1:100). Repeat the centrifugation and washing.
12. Dissolve the precipitate in 10 ml of conc. hydrochloric acid. In order to make the dissolution more rapid, the centrifuge tube may be placed in a container with warm water. Do not allow the concentration of hydrogen chloride to decrease below 10*M* through evaporation losses.
13. Let the solution pass through the ion-exchange column. Rinse the centrifuge tube three times with conc. hydrochloric acid in portions of 10 ml, which are poured on to the ion-exchange column. When a portion of the solution has been poured on, wait until the drop-rate is fairly low before adding a further portion. Collect the effluents, add 5 ml of aluminium chloride solution and evaporate to 1 ml.
14. Dilute and transfer the solution to a 25-ml measuring flask, add 1 ml of ascorbic acid, and mix well. Add 2 ml of naphtharson, fill up to the mark with distilled water and mix well.
15. Measure the absorbance of the solution at a wavelength of 550 mμ against a reagent blank, which in 25 ml contains the same amounts of reagents and 5 ml of hydrochloric acid (1:9). A suitable amount of thorium taken for the photometric determination is 30–150 μg. If it is necessary to take only part of the effluent in order to obtain this amount of thorium, hydrochloric acid must be added, so that the test solution contains 0·5 ml of conc. hydrochloric acid in 25 ml.

* This reagent has been variously called Naphtharson, Thoron, Thorin, Thoronol and APANS. The authors prefer the name which refers to the reagent as a chemical compound irrespective of its different analytical uses. APANS, presumably derived from the rational name, arsono-phenyl-azo-naphtyl-disulphonic acid, might be equally acceptable, were it not that *Chemical Abstracts* prefers the rational name, hydroxy-disulphonaphthylazobenzene arsonic acid!

INVESTIGATIONS

Decomposition of thorium containing ores: One of the methods recommended for decomposition of thorium-containing ores is to sinter a mixture of the ore and sodium peroxide at 430°.[3] The sinter cake is then digested with water, the solution is filtered, and the residue is washed and dissolved in strong hydrochloric acid. The thorium is assumed to be quantitatively dissolved. However, it is the authors' experience that this seldom is the case, when the method is applied to ores having a low thorium content, and chiefly consisting of silicates of a very variable composition. Only when the residue is sintered with sodium peroxide, and the residue thus obtained is sintered in its turn, does the recovery of thorium exceed 90%.

The thorium peroxide hydrate is difficult to dissolve quantitatively from the filter paper. It is therefore suggested that centrifugation should be used instead of filtration, after the third sintering with sodium peroxide.

As model experiments, some attempts were made to decompose different mixtures of Fe_2O_3 and Al_2O_3 containing between 0·3% and 1% of ThO_2. These were sintered with a large excess of sodium peroxide. The sinter-cake was digested with water. The insoluble residue was collected on a retentive filter paper, washed with 1% sodium hydroxide and treated with warm 6*M* hydrochloric acid. The filter was ignited, and the ash thus obtained was treated in the same manner as the original sample. This procedure was repeated once more. After each digestion the dissolved thorium was determined. These experiments showed that the losses of thorium after only one sintering with sodium peroxide were very great. (Table I).

TABLE I. PERCENTAGE OF THE TOTAL QUANTITY OF THORIUM FOUND

Decomposition number		
1	2	3
58	27	4
53	42	
57	40	
55	36	4
58	32	
56	30	8
54	34	2
73	23	

Elements interfering with the spectrophotometric determination of thorium: The decomposition with sodium peroxide and the following separation with the aid of a strongly basic anion-exchange resin will not lead to a complete separation of the thorium ion from other ions. Some of these interfere when thorium is determined with naphtharson. These ions are: phosphate ions,[1,3,4] ions of the rare-earth metals,[1,3,4] and nickel ion.

When phosphate is present in the original sample, small amounts tend to follow the thorium and might give rise to errors. A series of spectrophotometric determinations of thorium in the presence of different amounts of Na_2HPO_4 were made (Table II). It was found that the resulting variable errors could be suppressed to a large degree by the addition of aluminium ion (Table II). In the absence of phosphate, aluminium causes a positive error (Table III).

Some further experiments were made under conditions similar to those existing when analysing according to the procedure given above. To conc. hydrochloric acid, 10·7 or 43·3 μg of thorium and varying amounts of phosphate and aluminium were added. Some of the solutions were evaporated to 1 ml and others to dryness. The dry residues were dissolved in 1 ml of HCl (1:1). The solutions obtained in these two ways were treated in the same manner as the effluents (Operation 14–15). The results are given in Table IV. As will be seen from these, considerable losses of thorium occurred in the cases where no aluminium salt had been added, particularly when the solution was evaporated to dryness.

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TABLE II

Added		No Al added		10 mg Al added	
Th, *μg*	PO_4, *mg*	Th found, *μg*	Error, %	Th found, *μg*	Error, %
8·6	0·00	8·6	0	8·6	0
8·6	0·09	—	—	8·6	0
8·6	0·18	8·7	+1·2	8·6	0
8·6	0·27	4·9	−42·9	8·6	0
8·6	0·45	6·7	−22·0	8·7	+1·2
8·6	0·63	8·4	−2·3	8·7	+1·2
8·6	0·90	7·1	−17·4	8·5	−1·2
51·1	0·00	51·2	+0·2	51·3	+0·4
51·1	0·09	40·5	−20·8	51·1	0
51·1	0·18	16·6	−67·6	50·8	−0·6
51·1	0·27	37·7	−26·3	50·8	−0·6
51·1	0·45	47·2	−7·6	50·9	−0·4
51·1	0·63	42·7	−16·5	50·5	−1·2
51·1	0·90	29·4	−42·5	50·2	−1·8

TABLE III

Added		Found	Error
Th, *μg*	Al, *mg*	"Th", *μg*	%
8·0	0	8·0	0
8·0	5	8·1	+1·3
8·0	10	8·4	+5·0
8·0	20	8·7	+8·8
8·0	40	9·6	+20·0
8·0	80	10·5	+31·3
49·5	0	49·5	0
49·5	5	49·8	+0·6
49·5	10	50·3	+1·6
49·5	20	50·5	+2·0
49·5	40	52·3	+5·7
49·5	80	52·3	+5·7

TABLE IV

Added			Thorium found, *μg*			
Th, *μg*	PO_4, *mg*	HCl conc., *ml*	No Al added, solution evaporated to dryness	No Al added, solution evaporated to 1 ml	5 mg Al added, solution evaporated to dryness	5 mg Al added, solution evaporated to 1 ml
10·7	0·1	10	10·2	10·7	10·7; 10·5	10·9; 10·8
10·7	0·3	10	9·1	10·2	10·7; 10·0	10·7; 10·7
43·3	0·1	10	26·1	42·1	43·1; 43·3	43·2
43·3	0·3	10	22·6	41·4	42·4; 43·3	43·0; 43·3

The ions of the rare-earth metals are not retained by the anion-exchange resin[10] and as they interfere with the spectrophotometric determination of thorium the influence of the chief representatives of the rare earth elements, yttrium, lanthanum and cerium was studied. The errors are positive: 1 mg of La or Ce corresponds roughly to 2 μg of Th and 1 mg of Y to 0·4 μg of Th.

Nickel forms no chloro-complexes which can be adsorbed by the anion-exchange resin.[11] The interference of nickel in the spectrophotometric determination of thorium was studied (Table V). One mg of nickel gives a positive error corresponding to approximately 0·2 μg Th.

TABLE V

Added		Absorbance	Error, %
Th, μg	Ni, mg		
42	—	0·566	—
42	2	0·570	+0·7
42	5	0·579	+2·3
42	10	0·593	+4·8

Nickel can be separated from thorium in hydrochloric acid solution by the precipitation of the thorium with ammonia (Operation 9–12). According to Hecht and Grunwald[12] the precipitation of thorium hydroxide caused by ammonia is not quantitative on account of the formation of colloidal solutions. The addition of hydrogen peroxide to the ammonia solution gives thorium peroxide hydrate, which has not this disadvantage.

RESULTS

To check the accuracy of the procedure, thorium was determined in the presence of several elements. Mixtures were prepared containing elements which were expected to be encountered in our analyses of low-grade thorium-bearing minerals and ores. In a series of experiments, various oxides and salts were milled together, and a 100-mg sample of the mixture was decomposed by sodium peroxide. The sinter-cake was digested with water. To the alkaline solution a known amount of thorium was added in the form of a nitrate solution. The analytical procedure was then followed beginning with Operation 4. Table VI contains the results.

As a further test of the method, thorium was determined in some minerals. Their thorium content had been determined after the removal of interfering elements, using a more efficient but more time-consuming separation method. The sample was decomposed by hydrofluoric and sulphuric acids, and the residue was melted with potassium hydroxide. The melt was dissolved in water, and nitric acid was added. The two solutions thus obtained were combined and made alkaline with carbonate-free ammonia. The precipitate formed was dissolved in nitric acid. A chromatographic separation of thorium (and uranium) on alumina and cellulose was made according to Williams,[13] using ether containing 12·5% nitric acid as solvent. The effluent was evaporated to dryness, and the residue was treated with a mixture of sulphuric, nitric and perchloric acids, with heating, until the acids were driven off. The residue was dissolved in conc. hydrochloric acid. In order to separate thorium from uranium, and from small amounts of zirconium, the solution was poured on to a column of the anion-exchange resin Dowex 1—X 10. From this point the present procedure was followed. The results of the two procedures agree satisfactorily (Table VII).

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TABLE VI

Composition of mixture	Thorium added %	Thorium found %
10% U_3O_8, 9% ZrO_2, 13·5% Fe_2O_3, 9% Al_2O_3, 2·25% ZnO, 2·25% $BaCO_3$, 4·5% CaO, 4·5% MgO, 4·5% K_2SO_4, 9% $Na_2HPO_4 \cdot 2H_2O$, 31·5% SiO_2	0·015	0·015
	0·041	0·041
	0·083	0·084
	0·41	0·42
	0·42	0·42
	0·83	0·81
	0·83	0·84
	8·34	8·24
16·5% TiO_2, 8·3% U_3O_8, 7·5% ZrO_2, 11·3% Fe_2O_3, 7·5% Al_2O_3, 1·8% ZnO, 1·8% $BaCO_3$, 3·8% CaO, 3·8% MgO, 3·8% K_2SO_4, 8·4% $Na_2HPO_4 \cdot 2H_2O$, 26% SiO_2	0·015	0·016
	0·042	0·045
	0·083	0·084
16·1% Nb_2O_5, 3·2% Ta_2O_5, 13·3% TiO_2, 6·7% U_3O_8, 6·0% ZrO_2, 9·1% Fe_2O_3, 6·0% Al_2O_3, 1·5% ZnO, 1·5% $BaCO_3$, 3·1% CaO, 3·1% MgO, 3·1% K_2SO_4, 6·8% $Na_2HPO_4 \cdot 2H_2O$, 21% SiO_2	0·042	*
	0·42	0·40
	4·20	4·21
8·3% PbO, 8·3% V_2O_5, 13·4% Nb_2O_5, 2·7% Ta_2O_5, 11·1% TiO_2, 5·4% U_3O_8, 5% ZrO_2, 7·6% Fe_2O_3, 5% Al_2O_3, 1·3% ZnO, 1·3% $BaCO_3$, 2·6% CaO, 2·6% MgO, 2·6% K_2SO_4, 5·7% $Na_2HPO_4 \cdot 2H_2O$, 17·5% SiO_2	0·042	*
	0·42	0·40
	4·20	4·00

* A turbidity occurred on the addition of naphtharson.

TABLE VII

Mineral	Thorium found	
	This procedure, %	Cellulose chromatography, %
Silicates + uraninite	0·0026	0·0026
Pitchblende	0·0052	0·0061
Silicates + uraninite + + vanadium ore	0·0036	0·0026
	0·0034	0·0026
		0·0026
Mineral containing 29% Nb_2O_5, 21% rare earths, 16% TiO_2 and 13% U_3O_8	1·05	0·97
	0·94	0·98
Mineral containing 20% Nb_2O_5, 28% rare earths, 29% TiO_2 and 8% U_3O_8	2·89	2·95
	2·88	2·96
Mineral containing 40% Nb_2O_5, 4% Ta_2O_5, 12% rare earths and 0·5% TiO_2	1·02	0·98
	0·98	0·96
Mineral containing 46% ZrO_2 + HfO_2, 5·8% rare earths and 5·5% U_3O_8	1·49	1·52
		1·52
Mineral with unknown composition	0·12	0·14
	0·11	0·14

Zusammenfassung—Eine Methode zur Bestimmung von Mikrogrammengen Thorium in Mineralen und Erzen wird beschrieben. Die Mineralprobe wird durch wiederholtes Sintern mit Natriumperoxyd zersetzt. Nach Digestion mit Wasser wird das hydratisierte Thoriumperoxyd durch Zentrifugieren abgetrennt und in Salzsäure gelöst. Thorium wird dann spektrophotometrisch mit dem Natriumsalz der 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulfonsäure (Naphtharson) bestimmt, nachdem es von Metallen, die Chlorokomplexe bilden, in einer stark basischen Anionenaus-tauschersäule separiert geworden ist. Verschiedene Störungen wurden studiert. Die zur Durchführung einer Analyse benötigte Zeit ist etwa vier Stunden, wenn 12 Proben gleichzeitig behandelt werden.

Résumé—Les auteurs proposent une méthode de dosage de microgrammes de thorium dans des échantillons de minerals. L'échantillon est décomposé par frittage avec du peroxyde de sodium. Après digestion par de l'eau, le peroxyde de thorium hydraté est récupéré par centrifugation et dissous dans de l'acide chlorhydrique. Le thorium est dosé par spectrophotométrie par le sel de sodium de l'acide 1-(*o*-arsénophénylazo)-2-naphtol-3,6-disulfonique (naphtarson), après avoir été séparé des métaux qui forment des complexes chlorés; ces complexes sont adsorbés sur une résine échangeuse d'anions fortement basique. Les interférences de différents ions ont été étudiées. Le temps nécessaire pour l'analyse d'un échantillon est d'environ 4 heures, quand 12 échantillons sont analysés simultanément.

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APPLICATIONS DE LA CHELATOMETRIE—IX.

SEMI-MICRODOSAGE DE L'IODE DANS LES SUBSTANCES ORGANIQUES EN PRESENCE DES AUTRES HALOGENES

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Résumé—Aprés une minéralisation dans une microbombe suivant Wurzschmitt ou dans une fiole d'oxygène suivant Schöniger-Corner, l'iode combiné dans les substances organiques peut être précipité par un sel de palladium en solution titrée dont on mesure l'excés par chélatométrie.

INTRODUCTION

LES procédés volumétriques classiques les plus courants pour doser l'iode en présence des autres halogènes consistent, aprés une minéralisation convenable dans le cas des substances organiques, à oxyder les iodures en iode ou iodates de façon à permettre une évaluation par un thiosulfate ou par l'acide arsénieux[1–13,15,19,30–33] ou, encore, par l'antipyrine.[20]

De Sousa[21] a tout récemment utilisé une méthode chélatométrique afin de transformer en volumétrie le procédé gravimétrique de Bekk[22] pour le dosage des iodure et chlorure en présence l'un de l'autre: aprés une précipitation des halogénures d'argent, ceux-ci sont traités par le bichromate de potassium qui transforme l'iodure en iodate et le chlorure en chlore élémentaire; ce dernier est chassé par un courant d'air et l'iode est reprécipité à l'état d'iodure d'argent par réduction; aprés filtration et lavage à l'acide nitrique, ce sel est dosé par l'acide éthyléne-diaminotétracétique en présence de tétracyanonickelate de potassium et de murexide.

C'est également une méthode chélatométrique que nous avons mis en oeuvre mais elle a été choisie de façon à ne nécessiter qu'une seule précipitation, celle-ci étant sélective des iodures. Winkler,[23,24] Scott,[25] Strebinger avec Pollak,[26] Bugbee[27] et Beamish avec Dale[28] ont successivement étudié la précipitation du palladium par l'ion iodure ou inversement et Kondo[29] en a déduit un procédé gravimétrique de l'iode dans les corps organiques: aprés minéralisation par le péroxyde de sodium dans une bombe, l'anion iodure présent est précipité à l'état d'iodure palladeux qu'on filtre aprés un repos de 24 heures, séche à poids constant et pése.

Nous nous sommes basés sur le même principe pour établir un procédé volumétrique: aprés une minéralisation suivant la technique de Wurzschmitt[14,15] dans une microbombe de 2 ml en platine[18] ou suivant la technique de Schoniger[16,17] dans une fiole d'oxygène, avec la modification de Corner[34,35] que nous avions déja mise à profit pour la détermination des halogénes,[18] l'iode, réduit ensuite à l'état d'iodure, est précipité au moyen d'une solution de sel palladeux en excés et de titre connu; aprés filtration, l'excés est évalué chélatométriquement.

Le dosage du palladium par l'acide éthyléne-diaminotétracétique a été décrit par plusieurs auteurs: McNevin et Kriege[36] utilisent une méthode modifiée de Harris et

Sweet[37] en présence de noir ériochrome T et d'un excés d'acide éthyléne-diaminotétracétique qui est titré à retour par un sel de zinc; Kinnunen et Merikanto remplacent le sel de zinc par un sel de manganèse[38] avec le même indicateur, par un sel de thorium ou de thallium en présence d'orangé de xylénol[40] ou par un sel de bismuth en présence de violet de pyrocatéchine;[38] ces mêmes auteurs[38] confirment un procédé de Flaschka[39] basé sur le déplacement du nickel de son complexe cyané, le tétracyanonickelate de potassium, suivi d'une évaluation de ce métal en présence de murexide; c'est cette dernière façon d'opérer que nous avons retenue pour la partie chélatométrique de la présente technique.

PARTIE EXPERIMENTALE

I. *Minéralisation d'aprés Wurtzschmitt*

Réactifs utilisés:

Péroxyde de sodium
Mono-éthyléne-glycol
Chlorhydrate d'hydrazine, 0,2*M*
Acide chlorhydrique pur exempt de cations
Chlorure Palladeux, 0,02*M*‡ ou nitrate.

Mode opératoire: Dans une microbombe de 2 ml en platine, on introduit dans l'ordre 40 mg de mono-éthyléne-glycol (2 gouttes), un poids p_1 de substance* et 2 grammes environ de péroxyde de sodium; on ferme la bombe et chauffe le fond avec une petite flamme jusqu'à perception du claquement habituel. On laisse refroidir puis ouvre et place le corps de la bombe dans un bécher avec 20 ml d'eau distillée aprés avoir rincé le couvercle plusieurs fois à l'eau distillée chaude; on porte progressivement à ébullition jusqu'à cessation du dégagement gazeux; on laisse refroidir et transvase dans une fiole jaugée de 100 ml en rinçant plusieurs fois tout le matériel; on ajoute avec précautions 5 ml d'acide chlorhydrique puis 5 ml de chlorhydrate d'hydrazine 0,02*M*; on ajuste, si besoin est, le pH au dessous de 1 par une nouvelle addition d'un peu d'acide chlorhydrique; on attend quelques minutes et ajoute 10 ml de chlorure (ou nitrate) palladeux 0,02*M*; on abandonne dans un endroit frais jusqu'au lendemain puis compléte à 100 ml au moyen d'eau distillée; on agite le tout et filtre; on préléve 25 ml du filtrat sur lesquels on effectue le dosage proprement dit comme indiqué plus loin (III).

II. *Minéralisation d'aprés Schöniger*

Réactifs utilisés:

Soude caustique, *N*
Eau oxygénée, 20 vol.
Chlorhydrate d'hydrazine
Acide chlorhydrique pur éxempt de cations
Chlorure Palladeux, 0,005*M*† ou nitrate
Oxygène.

Mode opératoire: On découpe une bande de 30 mm sur 24 dans un ruban cellulosique adhésif sans cendres; on place cette bande à plat, coté adhésif au dessus, et pose au centre une plus petite bande de papier filtre sans cendres de 25 mm sur 6; on enroule le tout sur lui-même de façon à obtenir

* On calcule p_1 de façon à ce qu'il contienne 1/5,000 atome-gr. d'iode sans toutefois dépasser un poids total de substance de 40 mg. Nous avons utilisé des petites capsules de gélatine pour les pesées.

† La molarité exacte de cette solution est elle-même déterminée par chélatométrie: on préléve 10 ml qu'on place dans une fiole d'Erlenmeyer et ajoute 10 ml de tétracyanonickelate de potassium 0,025 *M* (voir plus loin la préparation de ce réactif); on acidifie légèrement par addition d'acide chlorhydrique, attend quelques minutes pour que la substitution du palladium au nickel soit compléte puis ajoute 10 ml d'ammoniaque et quelques décigrammes de murexide 1%; on titre avec le chélate 0,004 *M* (voir plus loin) au moyen d'une burette de 50 ml jusqu'au virage au violet. La molarité est donnée par la formule:

$$N'_P = \frac{V_C \times N'_C}{10}$$

V_C = nombre de ml de chélate utilisé,
N'_C = molarité (ou nombre de mol/g par litre) de ce réactif.

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un cylindre de quelques millimétres de diamétre sur une hauteur de 24 mm, la bande de papier filtre étant placée du coté intérieur de l'enroulement. Les deux extrémités étant constituées uniquement par la matière cellulosique adhésive peuvent se fermer facilement par simple pression et pliage; on ferme d'abord une seule extrémité, pése le micro-récipient ainsi formé et ajoute la substance à peser à l'intérieur (les liquides sont immédiatement pompés par le papier filtre). On ferme la deuxième extrémité et plie le tout pour le réduire à une petite masse vaguement cubique de quelques millimétres de coté; une deuxième pesée donne par différence le poids p_2 de substance prisonnière.* On place la petite masse dans le panier d'une fiole de Schöniger de 500 ml avec une petite bande de papier filtre servant à l'allumage. On met dans le fond de la fiole 5 ml de soude N, ajoute 10 ml d'eau distillée puis une dizaine de gouttes d'eau oxygénée 20 vol.; on opére alors selon la technique de Schöniger[16,17] dans la fiole remplie d'oxygène, fermée et renversée doucement aprés mise à feu. Aprés combustion, on agite la fiole énergiquement puis enléve le bouchon en le rinçant de même que son panier avec un peu d'eau distillée. On transvase la totalité du liquide dans une fiole jaugée de 100 ml en Pyrex en rinçant plusieurs fois la fiole de combustion; on porte à ébullition jusqu'à cessation du dégagement gazeux; on laisse refroidir et ajoute avec précautions 1 ml d'acide chlorhydrique puis 1 ml de chlorhydrate d'hydrazine 0,2M; on ajuste, si besoin est, le pH au dessous de 1 par une nouvelle addition d'un peu d'acide chlorhydrique; on attend quelques minutes et ajoute 10 ml de chlorure (ou nitrate) palladeux 0,005M; on abandonne dans un endroit frais jusqu'au lendemain puis compléte à 100 ml au moyen d'eau distillée; on agite le tout et filtre; on préléve 50 ml du filtrat sur lesquels on effectue le dosage proprement dit comme indiqué ci-aprés (III).

III. Dosage proprement dit

Réactifs utilisés:

Tétracyanonickelate de potassium, 0·025M, on dissout 6,25 g d'acétate de nickel $(CH_3COO)_2Ni$, $4H_2O$ dans 300 ml d'eau distillée puis ajoute 100 ml d'ammoniaque et 10 mg de murexide; à cette solution on ajoute, jusqu'à virage précis au violet, une solution contenant 6,2 g de cyanure de potassium dans 500 ml d'eau distillée (on procéde d'abord par approximation sur les 9/10e de la solution nickelique et termine à la burette aprés avoir ajouté le dernier dixième de cette solution) on compléte le tout à un litre au moyen d'eau distillée.

Chélate 0,004M: nous avons appelé ainsi une solution préparée par dissolution de 1,5 g d'éthyléne-diaminotétracétate disodique dans un litre d'eau fraichement bouillie et distillée; on détermine la molarité de cette solution à partir d'un poids connu de magnésium ou de zinc métalliques chimiquement purs en utilisant le noir ériochrome T comme indicateur ou à partir d'une solution titrée de nitrate d'argent en présence du réactif ci-dessus et de murexide.

Murexide 1%: on pése 0,1 g de murexide, ajoute 10 g de chlorure d'ammonium bien sec et broye le tout intimement.

Mode opératoire: A la prise d'essai, légèrement tiédie, provenant de l'une des minéralisations précédemment décrites, on ajoute 10 ml de tétracyanonickelate de potassium 0,025M; on acidifie légérement si besoin est, attend quelques minutes puis ajoute 10 ml d'ammoniaque et quelques décigrammes de murexide 1%; on coule le chélate 0,004M au moyen d'une burette de 10 ml jusqu'au virage au violet.

L'indimole[41] d'iode, ou nombre de milliatome-g d'iode contenu dans 100 g de substance, est donné par la formule:

$$H_I = \frac{V \times 100}{p}$$

$V = (20 \times N'_P) - (8 \times N'_C \times V')$ dans la technique de Wurzschmitt,
$V = (20 \times N'_P) - (4 \times N'_C \times V')$ dans la technique de Schöniger,
V' = nombre de ml de chélate utilisé,
N'_C = molarité de ce réactif,
N'_P = molarité de la solution de chlorure (ou nitrate) palladeux,
$p = p_1$ ou p_2 suivant le cas (exprimé en grammes).

La teneur % en iode est donnée par la formule:

$$T_I = H_I \times 0{,}1269$$

* On calcule p_2 de façon à ce qu'il contienne 1/20,000 atome-gr. d'iode sans toutefois dépasser un poids total de substance de 10 mg.

RESULTATS OBTENUS

Nous avons expérimenté la technique décrite ci-dessus sur quelques produits organiques iodés en utilisant dans chaque cas l'une et l'autre des deux modes de minéralisation décrits; les résultats obtenus ont été réunis dans le tableau ci-aprés.

TABLEAU I.

Produit essayé	poids, *mg*	Indimole		Iode %		Déviation, %
		calculé	trouvé	calculé	trouvé	
Iodure de propyle	33,09 (A)	588	584	74,6	74,1	−0,7
	32,81 (A)	—	583	—	74,0	−0,8
	8,64 (B)	—	585	—	74,2	−0,5
	8,41 (B)	—	584	—	74,1	−0,7
Iodure de butyle	35,82 (A)	543	540	68,9	68,5	−0,5
	36,04 (A)	—	542	—	68,8	−0,2
	9,08 (B)	—	540	—	68,5	−0,5
	9,27 (B)	—	541	—	68,6	−0,4
Acide p. iodo-benzoique	38,89 (A)	403	401	51,1	50,9	−0,5
	39,23 (A)	—	399	—	50,6	−1,0
	9,31 (B)	—	400	—	50,7	−0,8
	9,18 (B)	—	401	—	50,9	−0,5
Chlorure de p. iodo-benzoyle	39,34 (A)	375	373	47,6	47,3	−0,5
	39,61 (A)	—	376	—	47,7	+0,3
	9,82 (B)	—	376	—	47,7	+0,3
	9,71 (B)	—	374	—	47,5	−0,3
p. iodo-chloro-benzene	39,39 (A)	419	416	53,2	52,8	−0,8
	39,68 (A)	—	415	—	52,7	−1,0
	9,77 (B)	—	415	—	52,7	−1,0
	9,90 (B)	—	417	—	52,9	−0,5
p. iodo-bromo-benzéne	39,42 (A)	353	352	44,8	44,7	−0,3
	39,59 (A)	—	350	—	44,4	−0,9
	9,80 (B)	—	351	—	44,5	−0,6
	9,61 (B)	—	350	—	44,4	−0,9

(A) minéralisation d'aprés Wurzschmitt.[14,15]
(B) minéralisation d'aprés Schöniger[16,17]–Corner.[34]

Summary—After decomposition in a microbomb according to Wurzschmitt or in a oxygen flask according to Schöniger-Corner, iodine bound in organic matter can be precipitated by means of standard palladium salt solution, the excess of which is measured chelatometrically.

Zusammenfassung—Nach Zersetzung in eine Mikrobombe nachfolgend Wurzschmitt oder in eine Oxygenefläschchen nachfolgend Schöniger-Corner, kann organisch gebundener Jod mit einer Palladium-salzlösung fallen, deren Uberschuss chelatometrisch gemessen wird.

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FLUOROMETRIC DETERMINATION OF ZIRCONIUM WITH QUERCETIN

SEPARATION OF INTERFERENCES BY EXTRACTION WITH TTA

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Summary—The fluorometric determination of microgram quantities of zirconium in the presence of milligram quantities of interfering elements (particularly iron, vanadium and titanium) is described. The method involves extraction of zirconium with 2-thenoyltrifluoroacetone and development of fluorescence with quercetin. A study of experimental variables is included. The precision of the method is ±4%.

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INTRODUCTION

SPECTROPHOTOMETRIC determination of small quantities of zirconium is usually accomplished by reaction with alizarin sulphonic acid[2] or quercetin.[5] As Geiger and Sandell have pointed out,[3] the former method suffers from a lack of selectivity and the latter from a lack of sensitivity.

Fluorometric methods for zirconium have been developed using flavanol[1] and morin[3] as reagents. Both methods show good sensitivity for the detection of submicrogram quantities of zirconium. Both methods also consider interferences due to fluorescent complexes formed by the reagent and foreign ions. The former method does not, however, consider interferences due to the formation of coloured, but non-fluorescent, complexes between the reagent and foreign ions. The latter method does consider such interferences to some extent, but would not be generally applicable to the determination of microgram quantities of zirconium in the presence of milligram quantities of elements like titanium and vanadium.

The present method uses quercetin as the fluorometric reagent, together with extraction of the zirconium by 2-thenoyltrifluoroacetone dissolved in xylene, the extraction being modified from the procedure of Moore.[7] Such an extraction procedure eliminates interferences due to iron, vanadium and titanium.

EXPERIMENTAL

Reagents and solutions

Zirconyl chloride: A stock solution was prepared by dissolving $ZrOCl \cdot 8H_2O$ in water containing a small amount of hydrochloric acid. The solution contained 461·0 μg/ml of zirconium. This solution was successively diluted with absolute ethanol to give a working solution containing 4·61 μg/ml of zirconium.

Quercetin: The quercetin was recrystallised twice from absolute ethanol. A stock solution was prepared by dissolving 35 mg of the purified reagent in 100 ml of absolute ethanol. The resulting solution was stable for several months.

2-*Thenoyltrifluoroacetone* (*TTA*): The TTA was obtained from Midcontinent Chemicals Corporation (341 E. Ohio Street, Chicago 11, Illinois) and was used without further purification. An extracting solution was prepared by dissolving 9 g of TTA in 100 ml of reagent-grade xylene.

* Work performed at Polychemicals Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Delaware, U.S.A.

Apparatus

All fluorescence measurements were performed on an Aminco-Bowman Spectrophotofluorometer, equipped with a 1P21 photomultiplier tube. Readings were taken either on the 0·1 or 0·03 scales as indicated in the calibration curve shown later. The exciting wavelength used was 440 mμ and the fluorescence was measured at 505 mμ.

Procedure

This procedure was used to analyse for zirconium in the presence of metallic impurities. A blank was run with each determination, to compensate for the fluorescence of the reagent, and this value was subtracted from each reading. The fluoresence of the blank determined the lower limit of sensitivity of the method. Because of the lack of reproducibility of the instrument on a day-to-day basis, a standard zirconium solution was always run with a group of samples and the readings obtained were compared with the standard.

The sample was dissolved in 10 ml of 2*N* HCl. This solution was extracted with 10·0 ml of TTA in xylene by shaking continuously for 10 min. The layers were separated and the TTA layer was diluted with 25 ml of xylene. The diluted TTA layer was then extracted with 5·00 ml of 12*N* HCl by shaking continuously for 15 min. The HCl layer was transferred to a 25-ml volumetric flask, 1·00 ml of the quercetin solution was added and the whole was diluted to volume with absolute ethanol. The solution was permitted to stand for 20 min before measurement.

RESULTS

Fig. 1 shows the fluorescence and excitation spectra for the zirconium-quercetin complex under the conditions used in the present investigation. The spectra are presented as recorded, without correction for variations in source intensity and photomultiplier response as a function of wavelength. The nature of the zirconium-quercetin

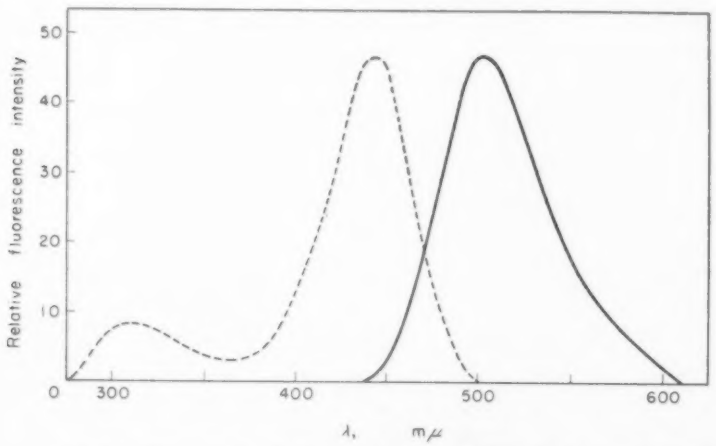

FIG. 1.—Fluorescence and excitation spectra of zirconium-quercetin complex. 20 μg of Zr, 0.35 mg quercetin in 25.00 ml of 2.4*M* HCl in ethanol.
——— fluorescence spectrum
- - - - - excitation spectrum

complex giving rise to fluorescence is not clearly established. Grimaldi and White[5] have reported that two complexes are formed in which the zirconium to quercetin ratios are 1:1 and 1:2. In the present investigation, a plot of fluorescence *vs.* mole fraction yielded a zirconium to quercetin ratio of 3:1. Under similar conditions,

La Para[6] found two breaks in a spectrophotometric continuous variations plot, at ratios of 3:1 and 1:1. The differences in environmental conditions among these studies may account for the differences observed, but the zirconium-quercetin system certainly merits further investigation.

Fig. 2 shows the calibration curve established for the fluorescence of the zirconium-quercetin system. It should be noted that the curve deviates from linearity at higher

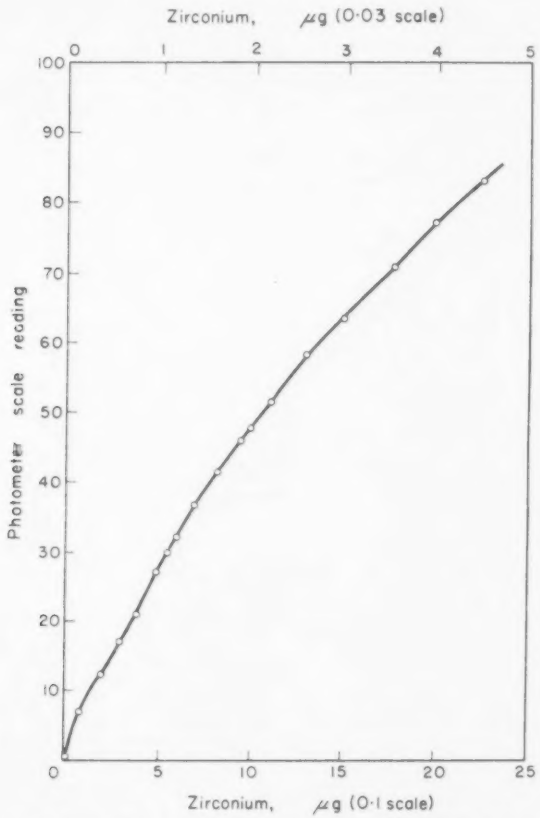

FIG. 2.—Calibration curve for zirconium determination solution. 0.35 mg of quercetin in 25.00 ml of 2.4*M* HCl in ethanol. Scales refer to setting of multiplier photometer.

zirconium concentrations, but this effect was not considered serious. Reproducibility of the method for the analysis of zirconium solutions was about 4%, relative, as shown in Table I. The results recorded in this table were taken over a period of several days, so that the variation includes that between days as well as between solutions. The lower limit of detection of zirconium was about 0·05 μg in 25 ml. The upper practical limit of the method (because of absorption of exciting radiation in the first small increment of solution arising from the intense colour of the complex) was about 75 μg in 25 ml.

It was necessary to remove interferences of other metal ions in the present method, particularly of vanadium and titanium. Although these metals do not form fluorescent

complexes with quercetin, they do form highly coloured complexes, in the present medium, which absorb over the same wavelength region as the zirconium-quercetin complex. When vanadium and titanium are present in milligram quantities, they absorb most of the exciting radiation in the first few mm of solution, completely eliminating the zirconium-quercetin fluorescence. Because of this, the zirconium was extracted with TTA and then re-extracted into 12*N* HCl. The extraction procedure used was not quantitative for zirconium, but the distribution coefficient was found to

TABLE I. REPRODUCIBILITY OF ZIRCONIUM ANALYSES WITH QUERCETIN

Zr taken, μg	Zr found, μg	Average $\pm$ s.d.	Relative error %
1·00	1·05 0·95 1·00 0·95	0·98 $\pm$ 0·05	5·2
4·61	4·65 4·60 4·80	4·68 $\pm$ 0·11	2·4
6·43	6·25 6·60 6·60	6·42 $\pm$ 0·22	3·5
9·22	9·05 9·20 9·60	9·28 $\pm$ 0·33	3·6
13·83	14·4 14·0 13·8	14·1 $\pm$ 0·4	2·8

TABLE II. EFFECT OF METAL IONS ON ZIRCONIUM DETERMINATION

	Solution containing 2 mg of Al, Ti, Mg, V^{V}, Fe^{III}		No interferences	
	Zr taken = 9·22 μg	Zr taken = 6·70 μg*	Zr taken = 9·22 μg	
Zr found, μg	10·1 9·20 8·55 9·00	6·30 6·70 6·55 6·40	9·60 9·65 9·00 10·2	
	$\bar{x}$ = 9·22 $\pm$ 0·58	$\bar{x}$ = 6·49 $\pm$ 0·18	$\bar{x}$ = 9·61 $\pm$ 0·49	

* Also contains 1 mg of Mn^{II}, Ni^{II}, Co^{II} and Cr^{III}.

be independent of zirconium concentration at these low zirconium levels. This allowed reproducible results to be obtained, although it reduced sensitivity. Measurements showed that about 90% of the original zirconium was recovered by this procedure.

Table II shows some typical analyses obtained by this method in the presence of a variety of metal ions. Combining the results of Moore[7] and of the present study, traces of zirconium can be determined successfully in the presence of the following ions: Al^{III}, Mg^{II}, Ti^{IV}, V^{V}, Fe^{III}, Sn^{II}, Ni^{II}, Co^{II}, Cr^{III}, UO_2^{++}, Th^{IV}, Fe^{II}, Bi^{III} and Nb^{V}. Although 2 mg of titanium cause no interference, some interference is encountered at higher levels. Such interference may be eliminated by adding 10 ml of 3% hydrogen peroxide to the initial extraction.

STUDY OF VARIABLES

Effect of alcohol concentration

It was observed that adding water to the zirconium-quercetin complex decreased the fluorescence. Fig. 3 illustrates this effect. Although the ethanol concentration is critical, reproducibility studies indicated that by carefully pipetting the 12*N* HCl used, a precision better than that of the overall method can be obtained.

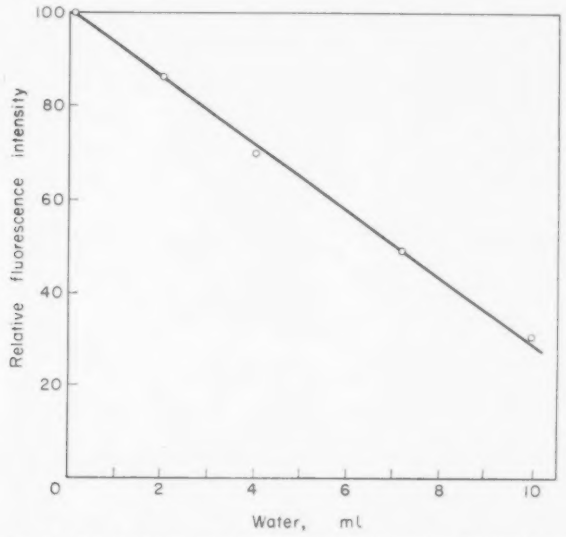

FIG. 3.—Effect of water on fluorescence of zirconium-quercetin complex. 10 μg of Zr, 0.35 mg quercetin in 25.00 ml of 2.4*M* HCl.

Effect of acid concentration

Solutions containing 20 μg of zirconium were treated with 1 ml of the quercetin solution and varying amounts of 6*N* hydrochloric acid in ethanol. Fig. 4 illustrates that acid concentration is quite critical, the fluorescence of the complex reaching its maximum in the vicinity of 2·5*M* HCl. Fortunately, the fluorescence does not fall rapidly on either side of the maximum and by adding the acid with a volumetric pipette one can obtain very reproducible results.

Effect of quercetin concentration

Solutions containing 20 μg of zirconium and 5 ml of 12*N* HCl were treated with varying amounts of quercetin. Fig. 5 illustrates that the optimum quercetin value fell at 0·35 mg/25 ml, which was equivalent to 1·00 ml of the quercetin stock solution. Here, also, the curve exhibits a broad maximum, indicating that small variations in the quercetin concentration will not adversely affect the analysis.

Effect of other variables

The other variables studied were the order of mixing and the time of standing after mixing. The order of mixing had no effect on the intensity of the fluorescence developed, but did affect the time required for the fluorescence to attain its maximum value.

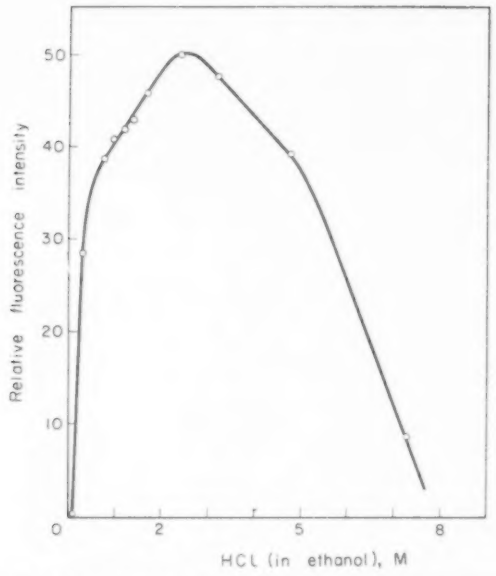

FIG. 4.—Effect of acid concentration on fluorescence of zirconium-quercetin complex. 20 μg of Zr, 0.35 mg quercetin in 25.00 ml of ethanol.

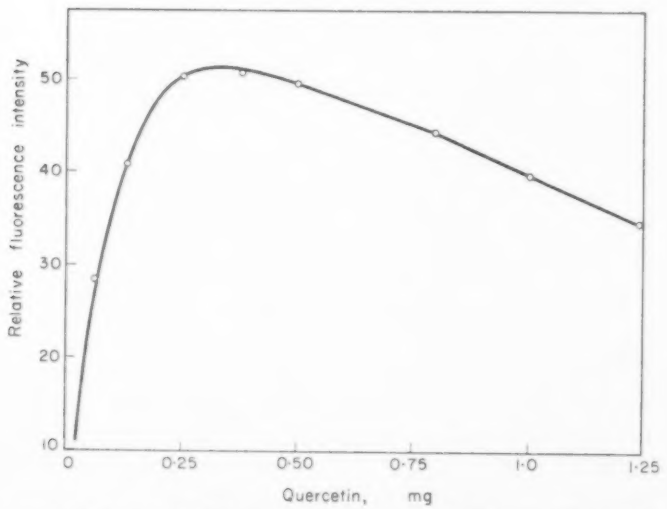

FIG. 5.—Effect of quercetin concentration on fluorescence of zirconium-quercetin complex. 20 μg Zr in 25.00 ml of 2.4*M* HCl in ethanol.

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For example, when the order of mixing was:

sample, quercetin, alcohol, acid

a period of 35 min was required to attain the maximum fluorescence. However, when the order of mixing was:

sample, acid, quercetin, alcohol

a maximum fluorescence intensity was obtained in 12 min. The final values obtained with the two orders of mixing were not significantly different.

Acknowledgement—The author wishes to express his thanks to Dr. Rolf Dessauer for his gift of quercetin and to Dr. D. R. Johnson for his helpful discussions.

Zusammenfassung—Die fluorometrische Bestimmung von Mikrogrammengen Zirkonium in Gegenwart von Milligrammengen störender Ionen (besonders Eisen, Vanadin und Titan) wird beschrieben. Die Methode beruht auf der Extraktion von Zirkonium mit 2-Theonyltrifluoroaceton und Erzeugung der Fluoreszenz mit Quercetin. Ein Studie der experimentellen Variablen wird mitgeteilt. Die Reproduzierbarkeit der Methode ist ±4%.

Résumé—L'auteur décrit le dosage fluorimétrique de quantités de l'ordre du microgramme de zirconium en présence de quantités de l'ordre du milligramme d'éléments gênants (en particulier fer, vanadium et titane). La méthode comporte l'extraction du zirconium par la 2-thénoyltrifluoroacétone et le développement de la fluorescence par la quercétine.

Une étude des variables expérimentales a été faite. La précision de la méthode est de ±4 pour cent.

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THE CONSECUTIVE RADIOMETRIC TITRATION OF SEVERAL ELEMENTS WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYL-PYRAZOLINE CONTAINING SULPHUR-35*

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Summary—The possibility has been demonstrated of the consecutive radiometric titration of a number of combinations of elements, such as Tl^{III}–In^{III}, Tl^{III}–Zn^{II} and Cd^{II}–Zn^{II}.

New forms of radiometric titration curves have been obtained.

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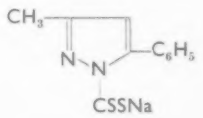
Organic precipitants containing radioactive isotopes deserve a more widespread application than they receive at the present time. We have used with success for this purpose the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazole, $C_{11}H_{10}N_2S_2Na$:



Like the derivatives of dithiocarbamic acid studied earlier, the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazole is capable of forming sparingly water-soluble compounds with a series of elements of the hydrogen sulphide and ammonium sulphide groups. The difference in the behaviour of the metal compounds formed is explained both by their dissimilar solubilities and by the dissimilar stabilities of the tartrates or other complexes of the metals at various pH values of the solution. By making use of this state of affairs it is possible to determine consecutively a series of elements simultaneously present by radiometric titration according to the precipitation method, unique titration curves being obtained. In this paper some examples are presented of the consecutive titration of two ions, of which one is completely precipitated from tartrate solutions at pH $\sim$ 14 and the other is precipitated only at lower pH values.

EXPERIMENTAL

Apparatus and reagents

The sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazole was synthesised by the method reported earlier,[1] starting from the corresponding pyrazole and carbon disulphide containing sulphur-35 with a specific activity of 13 mc/ml. The preparation obtained had a high specific activity which ensured an activity of about 1000 counts/min in the sample taken in the titration. Freshly prepared solutions were always used. Before dissolution, the reagent was dried in a desiccator over phosphorus

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† Student D. B. Sibiryakova took part in this work.

pentoxide. The normality of the solution was 0·01295*N* calculated from the weight of reagent taken and 0·01290*N* according to a thallium^{III} salt determination. The activity was measured with a type B instrument with a SBT-8 end-window tube. Before measuring the activity with respect to the γ-radiation of zinc-65, an aluminium filter with a thickness of ~2 mm was placed in front of the window. The equivalence point was found graphically. The solutions of thallium-204 and of stable thallium were prepared by dissolving the metals in *aqua regia*; then thallium^{III} hydroxide was precipitated, washed several times with water and dissolved in HNO_3. The other solutions were prepared by dissolving the appropriate metals in nitric acid.

Titration of thallium^{III} and indium^{III}

Into a centrifuge tube with a capacity of 50 ml were introduced a predetermined volume of titrated solutions of thallium^{III} and indium^{III}, a few ml of a 1% solution of NH_4Cl, an excess of a 5% aqueous sodium tartrate solution, and NaOH until the indicator tropeolin-00 changed to red or in an amount

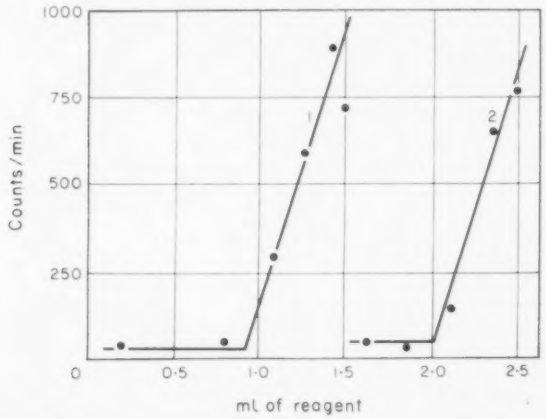

FIG. 1.—Curves for the consecutive radiometric titration of a 0·0044*N* solution of thallium^{III} and a 0·0045*N* solution of indium^{III} with a 0·05*N* solution of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline sodium salt containing sulphur-35: 1, titration of thallium; 2, titration of indium.

previously calculated to bring the pH to 14. The reagent solution was added from a 5-ml burette in separate portions; after separation of the precipitate by centrifuging, 0·01 ml of the solution was taken with a micropipette, deposited on filter paper and dried under an infrared lamp, and its activity was measured. In spite of the soft β-radiation of sulphur-35 (E_β = 0·1691 MeV), there was no need to introduce a correction for self-absorption. Since the sample taken was not put back, the amount of the ion being determined diminished somewhat during the titration, but since the volume of the solution titrated was relatively large (10–20 ml) and a minimum amount of solution was taken in the titration, the relative error does not exceed 1% which, in comparison with the error of the radiometric titration of ±5%, has little influence on the final results. Until the end-point of the titration is reached, the activity of the solution above the precipitate will be determined by the solubility of the thallium compound formed. After all the thallium has been precipitated, the activity of the solution increases with the addition of the reagent (Fig. 1, curve *1*). The completion of the reaction is also clearly observed visually from the cessation of the formation of the yellow precipitate of the thallium compound. On subsequent acidification of the solution to pH ~ 7 by the addition of acetic acid, with continuous agitation, the white indium compound begins to precipitate. On further addition of the reagent, the precipitation of the indium compound proceeds and the activity of the solution will be determined by the solubilities of the thallium and indium compounds. After all the thallium has been precipitated, the activity of the solution rises again (Fig. 1, curve *2*). The results of the titration are given in Table I.

Under favourable conditions it is possible, in principle, to titrate the ions of three metals successively.

Titration of thallium^{III} and zinc^{II}

Curves of a different type are obtained in the titration with a labelled reagent of two ions of which the one precipitating at the higher pH itself contains a radioactive isotope. As an example we shall consider the titration of thallium^{III} and zinc.^{II} The titration procedure was the same as in the previous case. To a standard solution of thallium^{III} was added an amount of the radioactive isotope ^{204}Tl, such that the activity of the sample taken in the titration was 1000–1200 cpm. On addition of the reagent, the activity of the solution above the precipitate will fall in consequence of the formation

Table I. Titration of thallium^{III} and indium^{III} with the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline containing sulphur-35

Tl added, *mg*	Tl found, *mg*	Error, %	In added, *mg*	In found, *mg*	Error, %
3·00	3·20	+6·66	0·50	0·46	−8·00
1·50	1·42	−5·34	3·00	2·94	−2·00
4·00	3·88	−3·00	2·00	2·09	+4·50
6·00	6·15	+2·50	1·50	1·43	−4·67

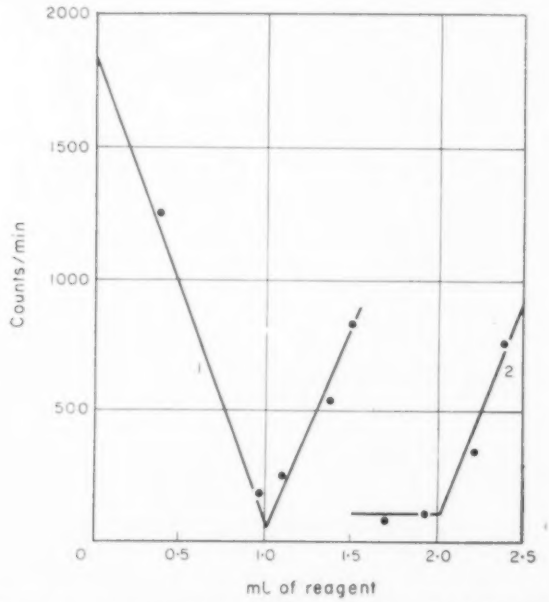

Fig. 2.—Curves for the consecutive radiometric titration of a 0·01*N* solution of ^{204}Tl^{III} and a 0·01*N* solution of zinc with a 0·05*N* solution of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline sodium salt containing sulphur-35: 1, titration of thallium; 2, titration of zinc

of the sparingly soluble thallium compound; after reaching the equivalence point, the activity of the solution will rise because of the activity of the reagent (Fig. 2, curve *1*). After lowering of the pH, the excess of reagent added will react with the zinc ion, and the activity will be determined by the solubility of the two precipitates containing the isotopes ^{204}Tl and ^{35}S.

After the equivalence point is reached, the activity rises and will be determined by the activity of the reagent (Fig. 2, curve *2*).

Titration of cadmium^{II} and zinc^{II}

When the cation precipitating second itself contains a radioactive isotope a somewhat different form of curve is obtained on titrating a mixture of cations with a labelled reagent. This situation

exists, for example, in the titration of solutions of cadmium and zinc containing the isotope ^{65}Zn with a solution of a labelled reagent. As can be seen from curve *1*, Fig. 3, as the cadmium precipitates the activity in the solution remains constant and depends on the radiation of the ^{65}Zn. After precipitation of all the cadmium and acidification of the solution to pH 7, the slight excess of reagent introduced reacts with the zinc and the activity of the solution above the precipitate diminishes. A decrease in

TABLE II. TITRATION OF THALLIUM-204^{III} AND ZINC WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYLPYRAZOLINE CONTAINING SULPHUR-35

Tl added, *mg*	Tl found, *mg*	Error, %	Zn added, *mg*	Zn found, *mg*	Error, %
3·0	2·8	−6·67	3·3	3·5	+6·06
3·0	2·7	−10·00	6·6	6·9	+4·54
3·0	3·2	+6·66	9·9	9·5	−4·05
6·0	5·6	−6·67	3·3	3·4	+3·03
9·0	8·2	−8·89	3·3	3·4	+3·03
3·0	3·1	+3·33	1·5	1·4	−6·67

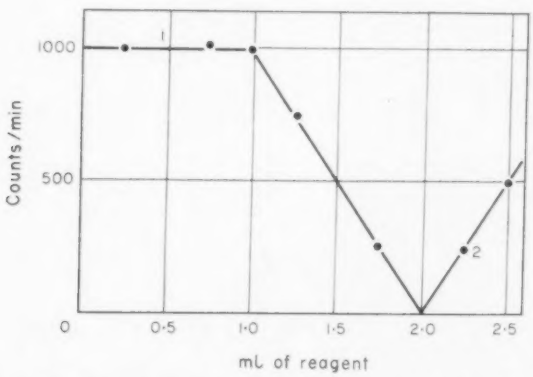

FIG. 3.—Curves for the consecutive radiometric titration of a 0·005*N* solution of zinc-65 and a 0·005*N* solution of cadmium with a 0·05*N* solution of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline sodium salt containing sulphur-35: 1, titration of cadmium; 2, titration of zinc.

TABLE III. TITRATION OF CADMIUM AND ZINC WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYLPYRAZOLINE CONTAINING SULPHUR-35

Cd taken, *mg*	Cd found, *mg*	Error, %	Zn taken, *mg*	Zn found, *mg*	Error, %
1·54	1·43	−7·14	10·70	9·50	−11·22
1·54	1·60	+3·83	4·20	4·05	−3·57
10·40	9·60	−7·70	4·20	3·80	−9·53
2·10	2·25	+7·14	13·20	12·70	−3·79

TABLE IV. DETERMINATION OF CADMIUM AND ZINC IN PHOSPHORS

Phosphors	Found, mean (of 6 titrations), %				Total ZnS + CdS in the phosphors, %
	Cd	CdS	Zn	ZnS	
19	7·49	9·62	60·52	90·17	99·79
14	8·22	10·85	59·03	87·91	98·76

the activity of the solution will be observed as long as all the zinc has not been precipitated. On addition of an excess of the reagent, the activity of the solution above the precipitate rises (measurement of the β-radiation of the sulphur-35). Thus, curve *2* in Fig. 3 gives the total amount of cadmium and zinc and curve *1* is a typical curve for a titration by the method of non-isotopic indicators.

Results of the determination of various amounts of zinc and cadmium are given in Table III.

Zinc and cadmium in phosphors based on ZnS and CdS have been determined in accordance with the methods described above (Table IV).

Zusammenfassung—Die Möglichkeiten Kombinationen von Elementen radiometrisch hintereinander zu titrieren werden aufgezeigt, wie z.B. die Systeme Thallium-Indium(III), Thallium(III)-Zink(II) oder Cadmium(II)-Zink(II). Neue Formen von radiometrischen Titrations-kurven werden gezeigt.

Résumé—Les auteurs montrent qu'il est possible de doser simultanément par radiométrie des combinaisons d'éléments telles que thallium(III)-indium(III), thallium(III)-zinc(II) et cadmium(II)-zinc(II). De nouvelles formes de courbes de titrage radiométriques sont présentées.

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APPLICATIONS OF INFRARED SPECTROSCOPY—V*

THE RETENTION OF WATER AND ORGANIC SOLVENTS BY CARBOHYDRATE MATERIALS

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Summary—Studies have been made of the extent to which some carbohydrate materials retain water and organic solvents. The water evolved was determined gravimetrically, the solvents by an infrared method. "Drying to constant weight" in an oven at 103°, or *in vacuo* at 80°, does not give true "moisture" contents. Both water and organic solvents are retained up to temperatures at which the carbohydrate materials begin to decompose: the polarity and boiling point of the solvent do not determine the extent to which it is retained. Freeze-dried samples can retain organic solvents, and have significant moisture contents. The possibility of inaccurate results and misleading artefacts arising from such retentions or from interaction with solvents is stressed.

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ORGANIC solvents are generally employed at some stage in the extraction or purification of carbohydrate materials. Thus, water-soluble polysaccharides are isolated, and plant gums purified, by precipitation from aqueous solution; Soxhlet extraction or refluxing with solvents removes plant pigments and soluble sugars, and inactivates enzymes; starches are "defatted" with 80% methanol or methanol-benzene, and are subsequently fractionated by the use of butan-1-ol or other polar organic solvents. The purified material is often "dried" by successive immersion in acetone, ethanol and ether, with final oven drying at temperatures slightly above the boiling points of the solvents used. Since such treatment may irreversibly decrease the solubility of some materials, *e.g.* starches, these are often stored under methanol or toluene until required.

The retention of moisture and organic solvents by pectins,[1] cellulose,[2] starches,[3,4] gum arabic[5] and biological polymers[6] has been reported: a mathematical treatment of moisture desorption isotherms has been given.[7] For cereals, "free water" (*i.e.* water lost at a stated drying temperature) has been distinguished[8] from "bound water", which is difficult to remove and is considered to be associated with the protein content. The effect of bound water has been considered in ultrasonic studies of hydration effects in sugars.[9]

In this paper we report quantitative observations on some polysaccharide materials in the belief that the extent to which retention of moisture and solvents can occur is not widely appreciated. The experiments were based on the use of a micro-scale, vapour-phase, quantitative infrared technique, developed recently[10] for the examination of fractions separated by GLC and used[11] for a study of the Zeisel alkoxyl reaction.

EXPERIMENTAL

Drying methods

Method I: Oven drying; temperatures and periods as stated.

Method II: Drying over phosphorus pentoxide in a conventional pistol-dryer, heated by refluxing organic solvent and evacuated by a water-pump.

* Part IV: D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 241.

Method III: Vacuum drying (usually at 80°) in a small electrically heated, thermostatted, glass drying chamber attached to a suitable high vacuum line (< 0·02 mm mercury pressure).

Method IV: Heating in a stream of dry nitrogen. The sample was weighed in a small 3-necked flask, which was then placed in a temperature-controlled oil-bath. The central neck of the flask carried a mercury thermometer pocket which was in contact with the sample. One of the two outer necks served as an inlet for CO_2-free nitrogen, dried by passage through Anhydrone; the third neck served as the outlet, to which was connected a tared Anhydrone absorption tube. This served in turn as the inlet to a cold trap immersed in liquid nitrogen. The outlet of the trap was fitted with an Anhydrone guard-tube (*cf.* ref. 11). The nitrogen flow-rate was 15 ml per min.

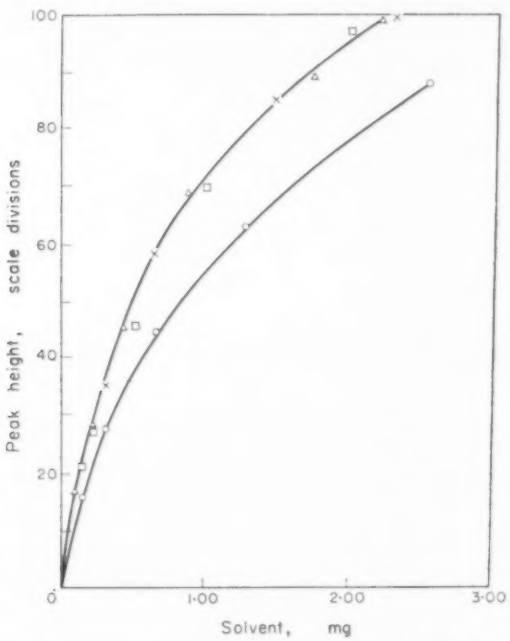

FIG. 1.—Infrared calibration curves for determination of solvents
○ Ethanol (1070 cm^{-1})
× Ether (1140 cm^{-1})
□ Acetone (1740 cm^{-1})
△ Methanol (1040 cm^{-1})

Determination of water released

The Anhydrone absorption tube was weighed at intervals. Anhydrone (B.D.H., M.A.R.) does not retain any of the solvents involved in these experiments.

Determination of organic solvents released

These were quantitatively retained in the cold-trap, and were subsequently determined by a quantitative vapour-phase infrared technique. This has been described,[10] together with details of the design of trap, method of quantitative transfer from trap to gas-cell, and methods of constructing calibration curves for each solvent involved (*cf.* ref. 11). The absorption peaks given by acetone at 1740 cm^{-1}, ethanol at 1070 cm^{-1}, methanol at 1040 cm^{-1}, and ether at 1140 cm^{-1} were used for calibration; the calibration curves obtained are shown in Fig. 1. (It is, of course, fortuitous that the sensitivity of detection of acetone, methanol and ether were all identical, as shown by their sharing a common calibration curve). No overlap or interaction occurred for the absorption peaks chosen, so that all four solvents could be determined simultaneously. The results from some typical experiments are reported below.

RESULTS

1. A sample of the gum from *Combretum leonense*[12] was precipitated with acidified acetone (0·1*N* with respect to HCl) and dried with 5 changes of acetone (each in contact for 2 days, the powder being progressively ground as it dried). The powder was stored in a desiccator (continuously evacuated) for 2 weeks at room temperature, and was then dried for 1 hr at 60° by method II. A weighed sample (554 mg) was then treated by method IV at various temperatures for lengths of time as shown in Table I. The total

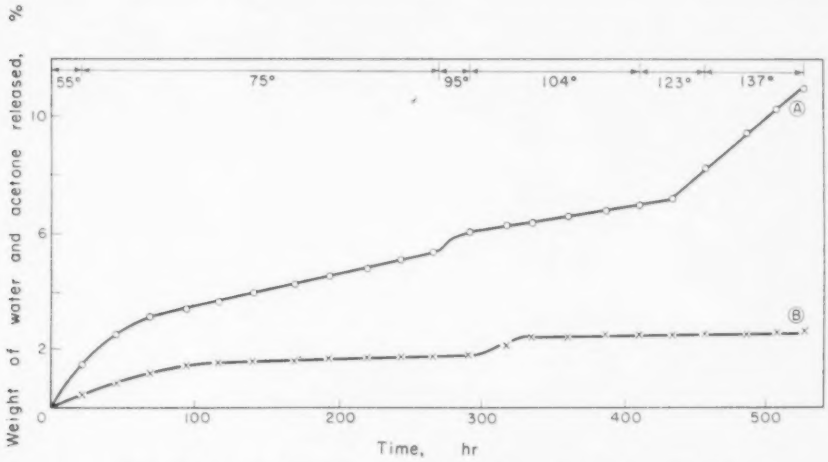

FIG. 2.—Release of water and acetone from a sample of *C. leonense* gum.
Curve OA—water
Curve OB—acetone

amounts of water and acetone evolved were found gravimetrically and spectrometrically respectively. Several measurements were made within each of the periods quoted in Table I; the results are shown graphically in Fig. 2. After heating for 525 hr, weight of gum recovered = 469 mg, *i.e.*, loss in weight = 85 mg. The weights of water

TABLE I

Period of heating, *hr*	Temp., *°C*	Total weight released from 554-mg sample.	
		water, *mg*	acetone, *mg*
1–20	55	7·9	2·2
20–264	75	29·2	9·8
264–288	95	33·0	10·0
288–406	104	38·5	12·3
406–454	123	46·3	13·1
454–525	137	60·0	14·3

+ acetone found total only 74·3 mg. Very slight decomposition of the gum began at 123° and was significant at 137°; in the period 430–525 hr (Fig. 2) 6 mg of CO_2 were evolved. This evolution of CO_2 would be accompanied by water produced in the decomposition, and this explains the sharp rise in the amount of total water released between 430 hr and 525 hr in Fig. 2.

2. Crude *C. leonense* gum was precipitated with acidified ethanol, dehydrated with 5 changes of acetone (as in 1 above) and finally washed with ether. After preliminary drying by method II for 6 hr at 60°, a weighed sample (474 mg) was dried by method IV at 70° for the period 1–5 hr, at 90° for 5–68 hr, at 105° for 68–116 hr, at 130° for 116–164 hr, at 140° for 164–188 hr, at 150° for 188–236 hr, and at 155° for 236–260 hr. The total weights of water, ether, ethanol and acetone liberated are shown graphically in Fig. 3. Decomposition of the gum was slight at 130° and pronounced at 140°: the graphs show that evolution of organic solvents continued steadily after the onset of

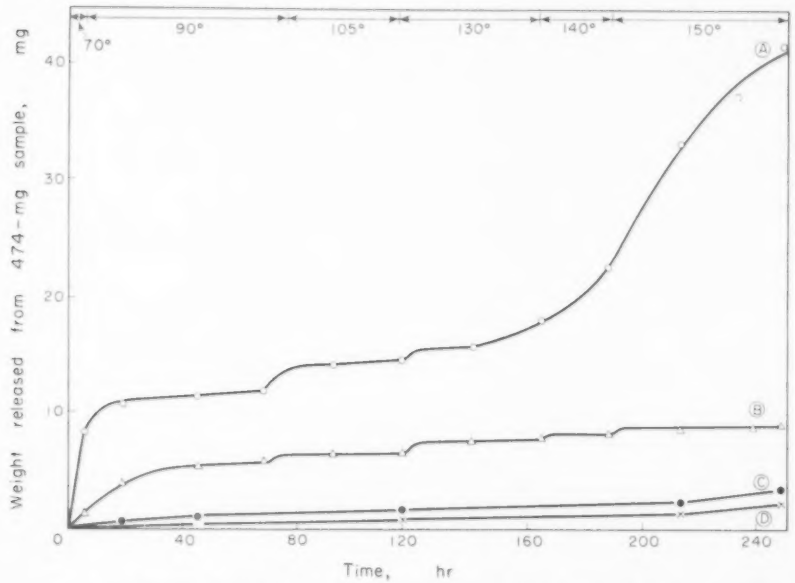

FIG. 3.—Release of water, ether, ethanol, and acetone from a sample of *C. leonense* gum.
Curve OA—water
Curve OB—ether
Curve OC—ethanol
Curve OD—acetone

decomposition. It is noteworthy that, of the three solvents involved, ether was the most strongly retained: this is surprising, since (*a*) its boiling point is the lowest, (*b*) it is the least polar, (*c*) it was used in smallest amount for the shortest contact time and only for superficial washing. Apparently the ethanol (used in the precipitation process) and the acetone (used in the dehydration procedure) are accessible to and extracted by the ether used in the final washing stage. This effect was verified in the next experiment.

3. A further sample of crude *C. leonense* gum was precipitated with acidified ethanol, dehydrated with absolute ethanol (5 changes, each in contact with the gum for 2 days), progressively ground to a powder, and finally washed with ether. After air drying, a weighed sample (845 mg) was dried by method II at 60° for 24 hr, when the total loss in weight (*i.e.*, water + solvents) was 3·5%, as represented by the curve OA given in Fig. 4. The sample was then quickly transferred and dried by method IV at 78° for a further 138 hr, *i.e.*, for the composite drying period of 24–162 hr. This gave part AB of the dehydration curve. Further drying at 108° for the period 162–234 hr gave curve BC; drying at 120° for period 234–258 hr gave curve CD. The dotted

curves AE, AF and AG give the weights evolved of water, ether and ethanol respectively; curve ABCD gives the sum of AE + AF + AG. The curves clearly show that solvents are still being liberated after drying for 280 hr, and confirm that the ether used as a final wash is more strongly retained than the ethanol used for both precipitation and dehydration.

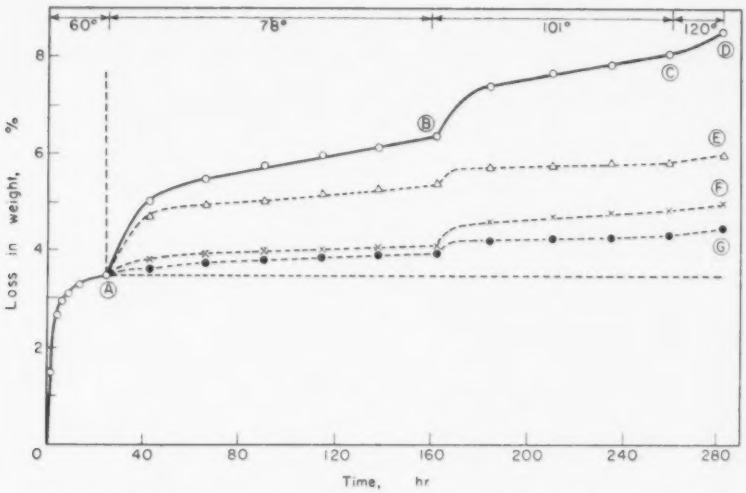

FIG. 4.—Release of water, ether, and ethanol from a sample of *C. leonense* gum.
Curve OABCD—total % loss in weight
Curve AE—water contributing to total AD
Curve AF—ether contributing to total AD
Curve AG—ethanol contributing to total AD

4. To test the effect of particle size on the retention, a sample of crude *C. leonense* gum was precipitated and dehydrated with methanol (6 changes, each in contact for 2 days). After air-drying, the sample was ground finely and sieved. Two fractions (*a*) passing 200 mesh and (*b*) passing 100 mesh were retained, and dried by method II at 60° for 9 hr. Weighed samples were then dried by method IV at 65° for the period 0–365 hr, at 95° for 365–437 hr, at 98° for 437–509 hr, and at 101° for 509–629 hr. For the 200-mesh sample, the weights of water and methanol evolved are given in Fig. 5 by curves *A* and *B* respectively, and for the 100-mesh sample by curves *C* and *D* respectively. These curves again emphasise that the drying temperature is more effective than the period of drying; methanol was still being released at the end of the experiment.

5. Parallel experiments to those described for *C. leonense* gum were made on samples of gum ghatti;[13] the retention of water and solvents by the two gums was very similar.

6. Further experiments were made with gum ghatti to test whether (*a*) solvents less polar than ethanol, methanol, acetone and ether *e.g.*, carbon disulphide and dioxan, or (*b*) solvents containing bulkier functional groups *e.g.*, isopropanol would be less strongly retained. For all of these solvents, however, retentions similar to those for acetone, ethanol, methanol and ether were given.

7. The retention of methanol by some starches was investigated. (*a*) A sample of potato starch (500 mg) was refluxed with methanol for 4 hr. After heating by method

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III at 80° for 24 hr, it was then dried by method IV at 98° for 0–18 hr, at 102° for 18–40 hr, at 108° for 40–64 hr, at 112° for 64–84 hr and at 134° for 84–88 hr. As much methanol was evolved in the final 4-hr period of heating at 134°, after steady evolution for 84 hr, as was evolved in the 18-hr initial period at 98°. (*b*) Rye starch, which had been stored under methanol at 0° for 2 years, was treated by method II at 61° for 24 hr.

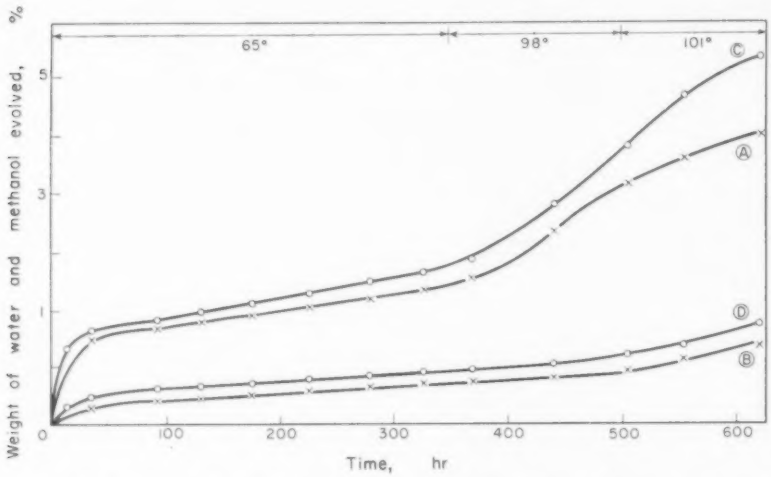

FIG. 5.—Effect of particle size on release of water and methanol from a sample of *C. leonense* gum.

Curve A—water, Curve B—methanol } from 200-mesh
Curve C—water, Curve D—methanol } from 100-mesh

A sample (500 mg) was then dried by method IV, the evolution of methanol being reported in Table II (+ and ++ indicate 0·1 — 0·5% and 0·5 — 1% w/w respectively). Similar results were obtained with other starch samples.

8. A sample of *C. leonense* gum which had been purified by ethanol precipitation, dialysed, and freeze-dried for 4 days was found to lose 1% by weight after heating at

TABLE II

Temperature, °C	78			92	98	115	128	140
Period of heating, *hr*	0–18	18–42	42–66	66–90	90–106	106–154	154–178	178–202
Methanol evolved	++	++	+	++	+	++	+	+

103° for 5 hr, and a further 1% on raising the temperature until decomposition began. Similar experiments with a freeze-dried sample of a pectic acid isolated from *Nitella translucens*[14] gave a loss in weight of 6·4% (duplicate runs) when the sample was taken direct from the freeze-drier; samples stored in a desiccator overnight after freeze-drying gave 8·5% loss in weight when treated by method III.

DISCUSSION

The results show that both water and organic solvents are retained tenaciously, even on prolonged drying under vacuum at temperatures much higher than the boiling point of the solvents concerned. Indeed, retention continues up to the temperature at which the polysaccharide material begins to decompose, as revealed by yellowing in colour and the starting of the evolution of CO_2. Furthermore, although apparent "constant weight" is reached after drying at a certain temperature for a determinable number of hours, continued drying at a slightly increased temperature gives further liberation of water and solvents, until eventually "constant weight" is again reached. This cycle can be repeated many times, by raising the temperature in small increments, until eventually the decomposition temperature of the carbohydrate material is reached.

Freeze-dried samples also retain moisture tenaciously, although in smaller amount; this agrees with Robson,[15] who found that a solution containing 16% glucose + 3% gelatin required freeze-drying for 500 hr at room temperature for *all* moisture to be removed. In practice, freeze-drying is not normally continued for longer than about 100 hr, and it is often assumed that samples so treated have a negligible moisture content: many quantitative inaccuracies must arise in this way. Freeze-dried samples may also retain organic solvents; cellulose retains 1·5% (w/w) of benzene on freeze-drying.[16]

Water and vapours can be occluded[17] in crystalline sugars; indeed, it was found recently[18] that when phenylboronate ester derivatives of methyl glycopyranosides were recrystallised from benzene, significant amounts of solvent were retained unless special care was taken to ensure its complete removal. Other authors[19] have recently reported similar solvent occlusion effects.

To obtain accurate quantitative results with carbohydrate materials, it is clear that great attention must be paid to drying procedures. Furthermore, any previous treatment of a sample with organic solvents must be considered if inaccurate and misleading functional group analyses *e.g.*, methoxyl, acetyl are to be avoided (*cf.* ref. 20). Application of the infrared alkoxyl method[11] has shown that mere reflux with ethanol can create artefacts *e.g.*, ethoxylation of the fructose from lucerne[21] and of certain plant gum components:[22] we are grateful to Dr. R. J. Ferrier for the information[18] that a dry, powdery xylan of normal appearance prepared by him contained 70% of ethanol. These findings serve to support the timely warning given by Bell[23] regarding the possibility of formation of non-reducing ethyl glycosides when plant materials are treated with hot 80–95% ethanol. It now appears likely that the occurrence of an ethyl riboside,[24] so far unconfirmed,[25] also arose in this way.

Acknowledgements—We thank Professor E. L. Hirst, C.B.E., F.R.S., for his interest in these studies, and the Department of Scientific and Industrial Research for a maintenance grant (to N. J. K.). We are grateful to Dr. R. S. Fanshawe, Dr. R. J. Ferrier and Dr. E. E. Percival for supplying materials for examination, and for providing experimental details.

Zusammenfassung—Es wurde untersucht, bis zu welchem Ausmasse einige Kohlenwasserstoffe Wasser und organische Lösemittel festhalten. Das Wasser wurde gravimetrisch und die Solventien mittels einer Infrarotmethode bestimmt. "Trocknen zu konstantem Gewicht" bei 103°C im Ofen oder bei 80°C im Vakuum gibt nicht den "wahren Feuchtigkeitsgehalt". Wasser sowohl als auch organische Lösemittel werden bis hinauf zu Temperaturen festgehalten, wo bereits Zersetzung der Kohlenwasserstoffe stattfindet. Polarität und Siedepunkt sind für das Ausmass der Retention nicht bestimmend. Frostgetrocknete Proben können organische Lösemittel zurückhalten und zeigen

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signifikante Gehalte und Feuchtigkeit. Die Möglichkeit ungenauer Ergebnisse und irreführenden Verhaltens, die durch diese Art von Retention hervorgerufen werden können, werden betont.

Résumé—Les auteurs ont étudié l'importance avec laquelle les hydrates de carbone retiennent l'eau et les solvants organiques. L'eau fixée était dosée par gravimétrie, les solvants par une méthode infra-rouge. Le "séchage à poids constant" dans un four à 103° ou sous vide à 80° ne donne pas des "teneurs en humidité" réelles. L'eau et les solvants organiques sont retenus tous les deux jusqu'à des températures auxquelles les hydrates de carbone commencent à se décomposer; la polarité et le point d'ébullition du solvant ne déterminent pas l'importance de sa liaison. Des échantillons séchés à froid peuvent retenir des solvants organiques et ont des teneurs en eau importantes. La possibilité de résultats inexacts et de produits aberrants provenant de fixation ou d'intéraction avec les solvants est soulignée.

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COLOUR REACTIONS OF SOME 1,4-DIHYDROXY-ANTHRAQUINONES WITH ALUMINIUM AND BERYLLIUM

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Summary—The colour reactions of 2-quinizarinsulphonic acid (sodium salt) and 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) with aluminium or beryllium have been studied and compared with the normal acid-base colour changes. pK values for these compounds were determined spectrophotometrically and compared with the ionisation of 1,2-dihydroxyanthraquinone-3-sulphonic acid (sodium salt). The application of the colour reactions of 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) with aluminium and beryllium to the spectrophotometric determination of both metallic ions is discussed.

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INTRODUCTION

SPECTROPHOTOMETRIC methods for the determination of aluminium using 2-quinizarinsulphonic acid (sodium salt), and of beryllium using 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt), have recently been developed in this laboratory.[10,11] This paper presents some of our results and views concerning the nature of the colour reactions of these compounds with aluminium and beryllium. The acid-base colour changes of the unreacted hydroxyanthraquinones show spectral resemblances to the colour changes which result upon reaction of these compounds with aluminium and beryllium. Hence the successful analytical use of these colour reactions for the determination of metallic ions depends on control of the normal acid-base reactions, and on recognition of the related problem of indicator salt effect. In general, as with most hydroxyanthraquinones, the reactions are very sensitive (1 part beryllium in 125,000,000 using 2-phenoxyquinizarindisulphonate) but they lack selectivity and are highly dependent on pH.

EXPERIMENTAL

Reagents

3-*Alizarinsulphonic acid* (*sodium salt*): The "indicator" grade of compound obtained from Allied Chemical and Dye Corporation was used after several recrystallisations from brine. Analysis: % C = 46·25, %H = 2·36 *vs* theoretical % C = 46·67, % H = 2·52.

2-*Quinizarinsulphonic acid* (*sodium salt*): About 90% pure.†

2-*Phenoxyquinizarin*-3,4′-*disulphonic acid* (*dipotassium salt*): About 90% pure.† Use a 0·1% solution in distilled water for the determination of beryllium or aluminium.

Standard aluminium solution: Dissolve about 1 g of accurately weighed pure aluminium metal in 20 ml of concentrated hydrochloric acid and dilute to 1 litre with distilled water. A trace of mercuric chloride added to the solution will increase the rate of solution. Make further dilutions of this standard solution as required.

Standard beryllium solution: Weigh accurately about 0·5 g of pure beryllium metal (Johnson, Matthey and Co.). Dissolve the metal in 250 ml of water with the addition of concentrated hydrochloric acid in an amount necessary to make the resulting solution 0·1*N* in acid when the solution is

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† The impurity consists of KCl or NaCl used in purification to salt out the compounds from aqueous solution.

diluted to 500 ml. Use a hood and avoid fumes. The pH of a 5-ppm solution prepared from this standard solution should be about 2.

Ca-EDTA sequestering agent: Dissolve 18·6 g of disodium EDTA and 12 g of calcium nitrate, $Ca(NO_3)_2.4\ H_2O$, in about 350 ml of water and adjust to pH 4·3 by adding about 6 ml of concentrated ammonium hydroxide. Dilute to 500 ml.

Cd-EDTA sequestering agent: Dissolve 9·3 g of disodium EDTA and 10 g of cadmium nitrate, $Cd(NO_3)_2.4H_2O$, in water, adjust to pH 3·5 and dilute to 500 ml.

RESULTS

Acid-base behaviour

The acid-base colour changes of 2-quinizarinsulphonic acid (sodium salt), 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) and 3-alizarinsulphonic acid

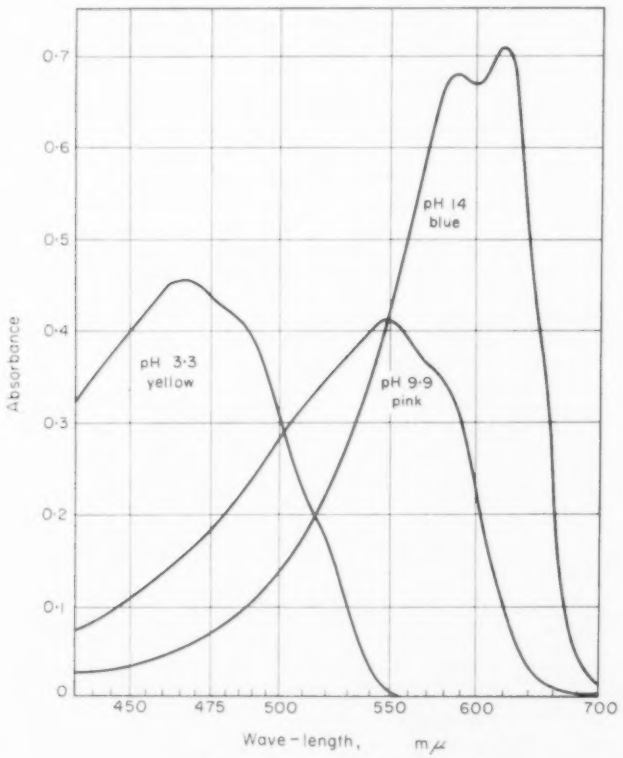

FIG. 1.—Effect of pH on spectra.
Spectra of $5{\cdot}54 \times 10^{-5} M$ 2-quinizarinsulphonic acid (sodium salt).

(sodium salt) are shown in Figs. 1–3. pK values of the acids were determined by plotting the absorbance at 470 mμ or 420 mμ versus pH. The mid-point of the inflection curve is assumed to be the point at which the two forms of the dye are equal. The graphs for the determinations of the pK values at an ionic strength of 0·1 at about 23° are shown in Figs. 4–6. Since the colour is not stable in basic solution, the pK_{a_2} values are more uncertain than pK_{a_1} values. Visually the second colour change from pink to blue is most pronounced with 2-quinizarinsulphonic acid (sodium salt). The

second colour change in the other two compounds is from pink to violet, being less apparent visually with 3-alizarinsulphonic acid (sodium salt).* The equations representing the acid-base behaviour of these compounds may be written thus:

$$H_2In \rightleftharpoons H^+ + HIn^- \ (1^{st} \text{ colour change})$$

$$HIn^- \rightleftharpoons H^+ + In^{-2} \ (2^{nd} \text{ colour change})$$

$$\text{In summary: } H_2In = H^+ + HIn^- = 2H^+ + In^{2-},$$

where In represents the indicator anion.

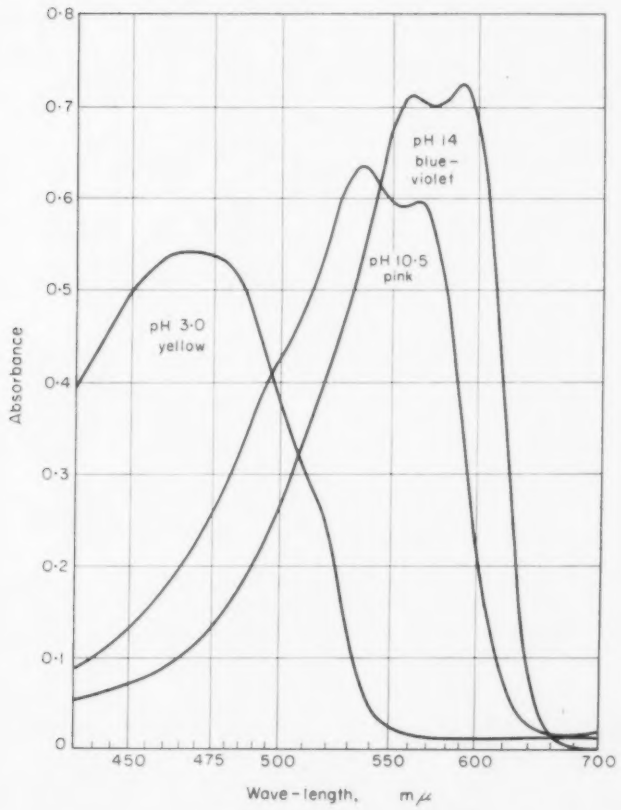

FIG. 2.—Effect of pH on spectra.
Spectra of $5{\cdot}54 \times 10^{-5}M$ 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt).

Then $$K_1 = \frac{[H^+][HIn^-]}{[H_2In]}, \text{ and } K_2 = \frac{[H^+][In^{2-}]}{[HIn^-]},$$

and $$pK_1 \text{ is the pH at which } [HIn^-] = [H_2In],$$

and $$pK_2 \text{ is the pH at which } [In^{2-}] = [HIn^-].$$

Results of the determinations are summarised in Table I. It is apparent from these values that 3-alizarinsulphonic acid (sodium salt) is a stronger acid than the 1,4-dihydroxycompounds. The pK_{a_1} value for alizarinsulphonic acid had been determined

* See ref. 12 for more details of this method of p*K* determination.

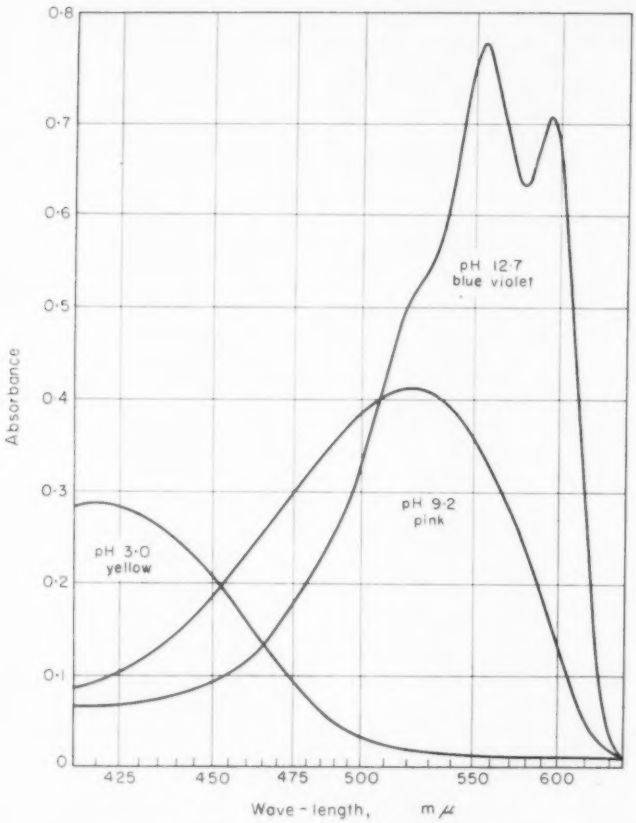

FIG. 3.—Effect of pH on spectra.
Spectra of $5{\cdot}54 \times 10^{-5} M$ 3-alizarinsulphonic acid (sodium salt).

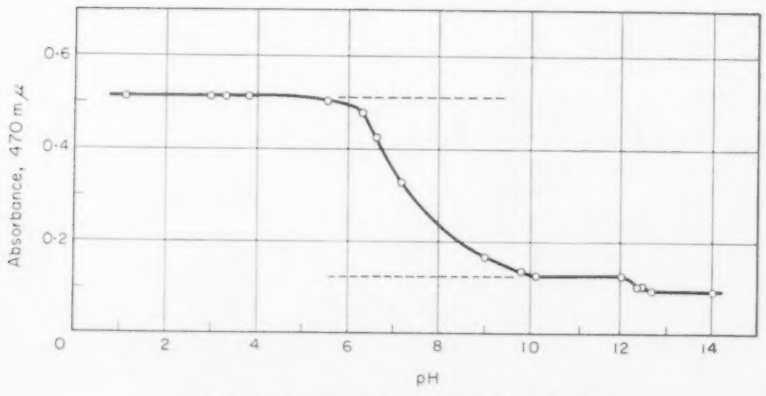

FIG. 4.—Spectrophotometric pK determination.
2-Phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt), $5{\cdot}54 \times 10^{-5} M$, ionic strength 0·1, 23°.

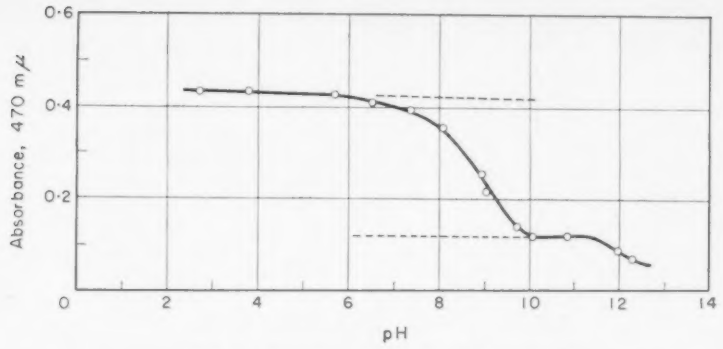

FIG. 5.—Spectrophotometric pK determination.
2-Quinizarinsulphonic acid (sodium salt), $5{\cdot}54 \times 10^{-5}M$, ionic strength 0·1, 23°.

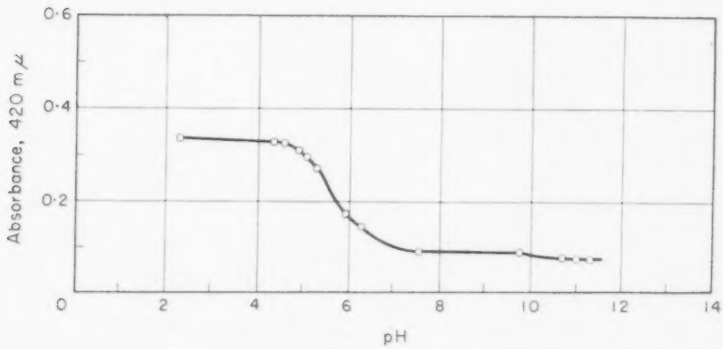

FIG. 6.—Spectrophotometric pK determination.
3-Alizarinsulphonic acid (sodium salt), $5{\cdot}54 \times 10^{-5}M$, ionic strength 0·1, 23°.

Table I.—pK Values at an ionic strength[a] of 0·1 at 23°

Compound	pK_{a_1}	pK_{a_2}
	[b]	[c]
2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt)	7·3 ± 0·1	about 12·4
2-quinizarinsulphonic acid (sodium salt)	8·7 ± 0·1	about 12
3-alizarinsulphonic acid (sodium salt)	5·7 ± 0·1	about 10·2

[a] With potassium nitrate, dye concentrations were $5{\cdot}54 \times 10^{5}M$.
[b] Accuracy of ± 0·1 pH unit has not been rigorously established with replicate determinations; however, in the single determinations the graphs can be interpreted within these limits.
[c] Uncertain because of instability of the compounds in basic solution.

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previously[1] as 8·14. However, this older value does not coincide with the colour change interval of alizarinsulphonate as found by us, and as listed in handbooks (colour change interval pH 3·7 to 5·2, yellow to violet).[8] Moreover, we find that in neutralisation curves using sodium hydroxide as titrant, alizarinsulphonic acid is bracketed in the criteria of sharpness of the equivalence point break by acetic acid (pK_1 4·6, $\mu = 0{\cdot}1$ at 25°) and disodium ethylenediaminetetra-acetic acid (pK_3 6·16, $\mu = 0{\cdot}1$ at 20°).[16] The mid-point in the titration of 0·008M alizarinsulphonic acid (sodium salt) with 0·1N sodium hydroxide occurred at about pH 6. (Ideally pH = pK_{a_1} at this point.) The difference between $pK = 5{\cdot}7$ and 6 is partly accounted for by the difference in ionic strength in the two determinations. This indicates that the colour change of alizarinsulphonic acid is coincidental with ionisation of a hydroxyl hydrogen. The first colour change of alizarinsulphonic acid (sodium salt) has been linked with hydrolysis of the sulphonic acid group by other investigators.[13] This assumption seems incorrect, inasmuch as sulphonic acids are relatively strong acids. Moreover, the colour changes of sulphonated alizarin are similar to the colour changes of unsulphonated alizarin.[2] Finally, the neutralisation curve of 2-quinizarinsulphonic acid (sodium salt), titrated with sodium hydroxide, showed only a very small inflection compared with the curves of disodium-EDTA, acetic acid, and alizarinsulphonic acid. This agrees with the spectrophotometric pK_1 value of 8·7. Since sulphonic acid groups in the two compounds are not expected to have widely different natures, the difference in pK values must result from a difference in type of hydroxyl hydrogens.

The difference in pK_1 values for 1,2-dihydroxyanthraquinone-3-sulphonic acid (sodium salt) and 1,4-dihydroxyanthraquinone-2-sulphonic acid (sodium salt) is 3·0. Assuming that the difference in measured equilibrium constants (at $5{\cdot}54 \times 10^{-5}M$ and $\mu = 0{\cdot}1$) closely approximates to the difference in the true equilibrium constants, and that entropy changes are not significantly different for the two reactions, the difference, ΔH, between the two reactions can be estimated. For ΔpK_1,

$$\Delta H = -RT \ln K$$
$$= 2{\cdot}3 \times 1{\cdot}987 \times 296 \times 3$$
$$= 4{\cdot}1 \text{ kcal. mole}^{-1}.$$

This is the right order of magnitude for the breaking of a hydrogen bond. Indeed, the difference between 1,4-dihydroxy and 1,2-dihydroxy compounds is that one posesses two intramolecularly bonded hydroxyl hydrogens and the other only one. This view is supported by infrared evidence[3] and further by differences in melting points in the various hydroxyanthraquinones. Dihydroxyanthraquinones, having only internally bonded hydroxyl groups, have significantly lower melting points. Hydrogen bonding is sterically posible between the sulphonic acid anion group and adjacent hydroxyl groups. Apparently this does not contribute much to the stability (ease of ionisation), especially with regard to pK_1. Green[4] found $pK_1 = 8{\cdot}2$ and $pK_2 = 10{\cdot}7$ for 6-quinizarinsulphonic acid (sodium salt). The sulphonic acid group is not adjacent to a hydroxyl group in this compound.

Nature of the Be-2-phenoxyquinizarin-3, 4′-disulphonic acid complex

Purification of the organic reagent was necessary because the crude product gave a sulphur analysis suggesting that it was a mixture of mono- and disulphonic acids.

Purification of the reagent: The commercial product (1·3 g) was recrystallised seven times from water by salting out with 2% potassium chloride. The purification was carried out by adding small amounts of potassium chloride solution and filtering off the insoluble precipitate. The insoluble portion was discarded and the filtrate used for further similar steps. In this manner, concentration of the more soluble component was effected. After seven purification steps the yield was 0·7 g. Analysis of the purified product for carbon, hydrogen, and residue showed the residue to be high and the carbon and hydrogen to be low based on theoretical calculations as the disulphonic salt. Assuming the excess residue to be potassium chloride (chloride was detected with silver nitrate in a portion of the residue, after igniting and dissolving the residue in water) the analysis could be reconciled. Under these assumptions, it was calculated that the compound was about 90% pure.

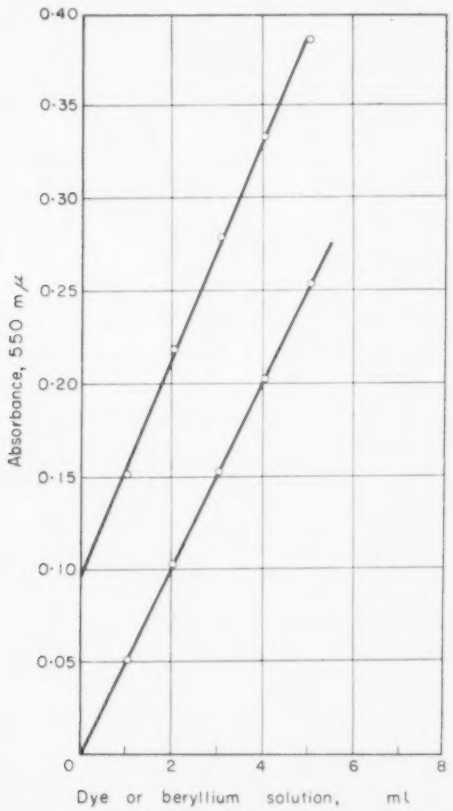


FIG. 7.—Mole ratio determination by the slope ratio method.
Curves result from adding small increments of either beryllium or 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) to an excess of the other component. (pH 6·5).

Determination of combining ratio: In confirmation of our assumptions, the mole ratio determinations showed a slight discrepancy in combining ratio which could be explained by the fact that the reagent was not 100% pure, *i.e.*, in the slope ratio method of Harvey and Manning[5] the combining ratio of dye to beryllium appears to be 1·13:1 (see Fig. 7). Correcting for 10% non-reactive impurity, the combining ratio of dye to beryllium is 1:1. Similar results indicating a 1:1 mole ratio were obtained with Job's continuous variations method[6] and the method of Yoe and Jones.[17]

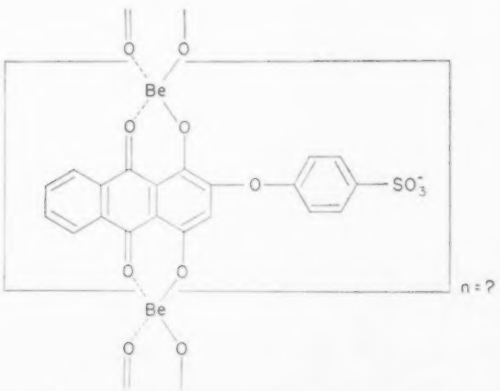
The absorption peaks of the complex in the presence of excess beryllium do not change significantly with pH, whereas the absorption peaks of the reagent do shift

(see Table II). This could indicate that a hydroxyl hydrogen present in the unreacted reagent at pH 6 is ionised at pH 6 in the beryllium complex. (It is possible that the formation of the beryllium complex changes the pK values for ionisation from that in the unreacted reagent). Assuming this to be true, a possible structure for the complex can be written which is analogous to a postulated structure for the 1:1 complex of beryllium and naphthazarin.[14] In the beryllium-naphthazarin 1:1 complex, two moles of hydrogen ions are liberated per mole of complex formed. There is no evidence that a

Table II.—Absorption peaks, mμ

	pH 6	pH 10·7
Complex with excess beryllium	488, **518**, 554	492, **522**, 564
Reagent alone: 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt)	**465**, 512	~490, **534**, 562

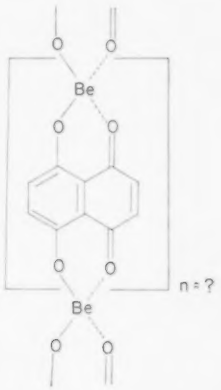
2:1 complex is formed between 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) and beryllium, although beryllium does form such a complex with naphthazarin.[14] Compared to naphthazarin, the phenoxyquinizarin molecule is certainly larger, but not, however, prohibitively so from the standpoint of steric hindrance, if a tetrahedral complex is assumed. Hence the reason why the 2:1 complex is not formed cannot be explained by an obvious steric reason. Under our conditions, *i.e.*, in 0·4M ammonium acetate the second ligand position may be occupied by an acetate ion if n = 1.



Be-phenoxyquinizarinsulphonate 1:1 complex

The similarity of the visible spectra of the complex to the spectra of the ionised form of the unreacted reagent may indicate that the formation of the metal-dye complex "induces" ionisation of the reagent. This would cause a premature colour change with respect to the pH at which it normally occurs in the acid-base reaction of the dye. A similar mechanism has been postulated for the thorium-alizarin S reaction.[9]

This complex could readily form a polymer, as shown in the structure of the beryllium-naphthazarin complex.



Be–naphthazarin 1:1 complex[14]

Whether or not a polymer is formed under the conditions of analysis is not known. The fact that Beer's law is not obeyed at high concentrations may indicate polymer formation. (Above 0·7 ppm the absorbance-concentration curve deviates towards the concentration axis). Non-additive absorbances in the case of mixtures of aluminium and beryllium are another indication of component interaction, possibly related to mixed polymer formation. Most of these considerations apply to the aluminium-phenoxyquinizarinsulphonate complex as well; however, the combining ratio has not been determined. In methanol, aluminium and 2-quinizarinsulphonic acid form a 1:1 complex.

Analytical behaviour of the Al-2-phenoxyquinizarin-3,4′-disulphonic acid complex

The effect of pH for the aluminium complex is shown in Fig. 8. The optimum value is pH 6·0, $\mu = 0{\cdot}1$. The complex forms rapidly after mixing, and the colour decreases in intensity as shown in Fig. 9. Nearly constant absorbance is reached after one hour. Beer's law is not obeyed, and the deviation is greater than that of the beryllium complex under the same conditions (see Fig. 10). Sensitivity for aluminium at the 0·2-ppm level is 0·0013 $\mu g.cm^{-2}$ for $\log I_0/I = 0{\cdot}001$. A more practical sensitivity however, is 1 part in 50,000,000.

Determination of both aluminium and beryllium with 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt)

Both aluminium and beryllium form pink-violet complexes with this reagent at pH 6. Absorption maxima are within the range 550–560 mμ. By using Ca-EDTA as a sequestering agent, it is possible to determine beryllium in the presence of aluminium by the method recently developed in this laboratory.[11] Since an independent measurement for beryllium is possible, an investigation was made to determine whether the sum of the two absorbances could be used to determine aluminium by difference.

Investigation of procedures

Two masking agents are used: Ca-EDTA for the separate determination of beryllium, and Cd-EDTA for determination of the sum (aluminium + beryllium). Cd-EDTA allows the aluminium

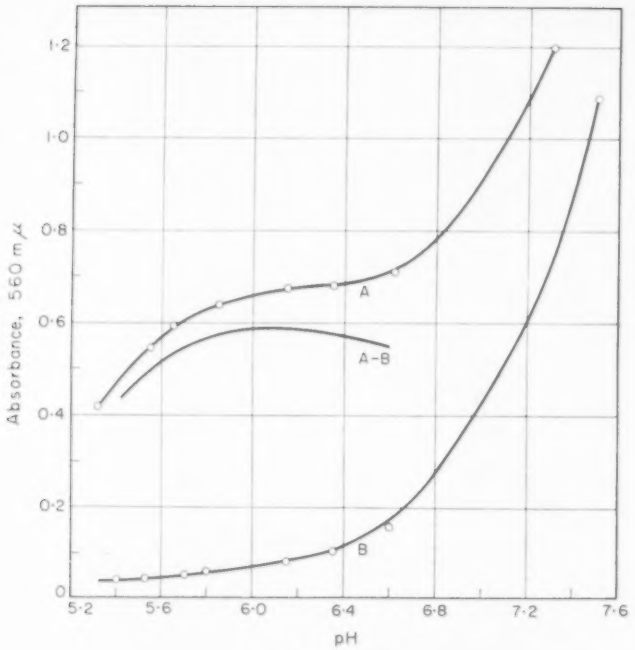


FIG. 8.—Effect of pH.
A. 1 ppm of aluminium in presence of B.
B. 0·1% 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt).
Cd-EDTA (0·01 *M*) and ammonium acetate (0·4 *M*) present in both A and B.

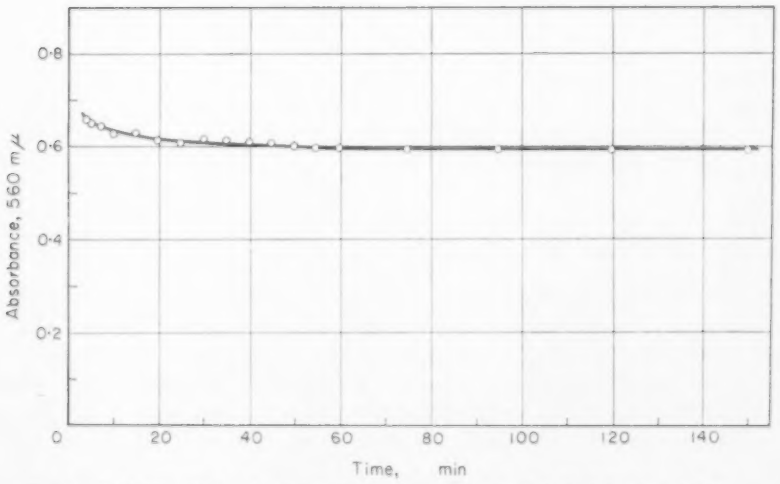


FIG. 9.—Stability of the aluminium-2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) complex with time.

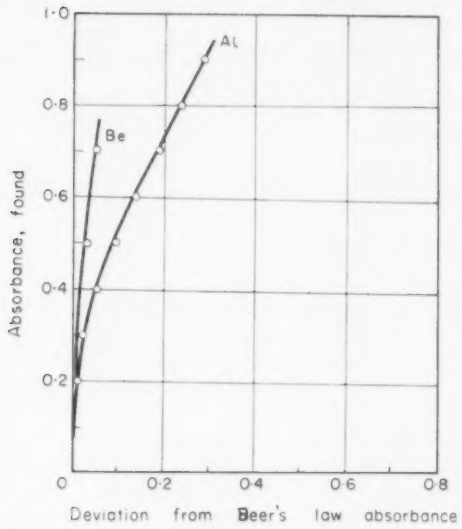


FIG. 10.—Beer's law deviation.
Aluminium and beryllium complexes with 2-phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt), Cd-EDTA (0·01*M*) and ammonium acetate (0·4*M*) present, pH 6·0.

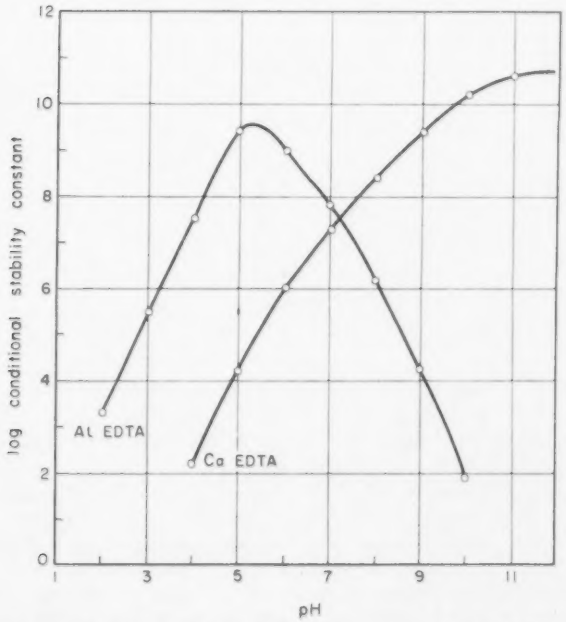


FIG. 11.—Effect of pH on conditional stability constants of metal-EDTA complexes.[7]

complex to develop but Ca-EDTA masks aluminium by exchange. This is explained by stability constant relationships of the EDTA complexes of the three metal ions (see Table III).

Table III.—EDTA conditional stability constants[7]

	pH 6	pH 8
Ca	6·0	8·4
Al	9·0	6·2
Cd	11·8	14·1

A variation of this technique was tried using aliquots of the same final solution. Cadmium ions were added to a portion of the sample solution containing aluminium masked by Ca-EDTA. Cadmium ions replaced calcium and aluminium ions. The demasking of aluminium in the presence of beryllium should result in a stepwise increase in absorbance. The "blank" using this procedure had a high absorbance because of the two-fold excess of cadmium ions added, as well as the liberated large excess of calcium ions.

Another possibility for demasking aluminium was to change the pH from 6 to 8. At pH 8 the relative stabilities of the Ca-EDTA and Al-EDTA complexes are reversed (see Fig. 11). This did not work out in practice. Moreover, the colour change of the dye occurring at pH 7·3 increases the "blank" absorbance. The first method using two solutions, one with Ca-EDTA as masking agent and

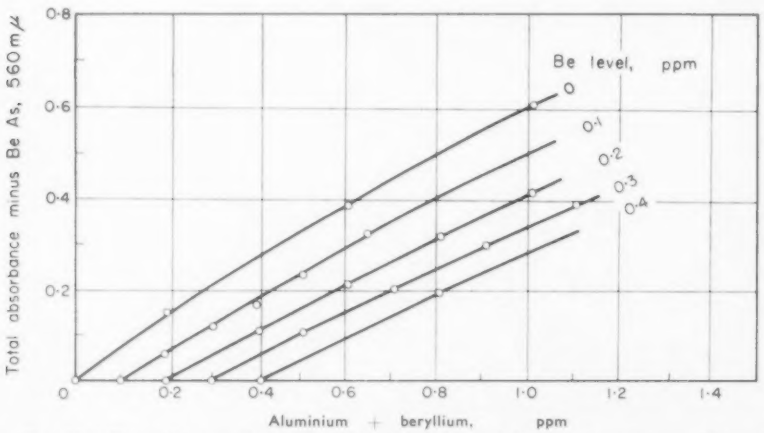


Fig. 12.—Correction graph for determination of aluminium in the presence of beryllium.

the other with Cd-EDTA as masking agent proved to be the best of the three trials. The aluminium and beryllium complexes do not obey Beer's law, which is a disadvantage; moreover, the system containing both ions behaves as if there were some variable interaction between aluminium and beryllium ions in solution. A correction graph was made from the results of a series of known solutions containing only aluminium and beryllium (Fig. 12). This graph can be used to determine aluminium in similar solutions with an accuracy of about ±10%, compared to ±2·5% for beryllium determined separately. Because of the non-additive nature of the two absorbances, the method is not recommended for the precise determination of aluminium in the presence of beryllium. Masking with Cd-EDTA is theoretically not as effective as with Ca-EDTA, because cadmium forms a stronger complex than calcium and will not be displaced as easily by interfering ions. Effects of foreign ions have not been investigated. It is recommended, however, that the aluminium and beryllium be isolated in a solution of the same general composition as that used to construct the correction graph. This would be practical, for example, after separation of foreign ions at the mercury cathode.

Zusammenfassung—Die Farbreaktionen von 2-Chinizarinsulfonsäure (Natriumsalz) und 2-Phenoxychinizarindisulfonsäure (Dikaliumsalz) mit Aluminium und Beryllium wurden studiert und mit den Säure-Basen-Farbumschlägen in Vergleich gesetzt. Die pK-Werte der Säuren wurden photometrisch bestimmt und mit denen der 1,2 Dioxyanthrachinon-3-sulfonsäure (Natriumsalz) verglichen. Die Farbreaktionen der 2-Phenoxychinizarin-3,4-disulfonsäure (Dikaliumsalz) mit Aluminium und Beryllium wurden zur photometrischen Bestimmung der beiden Metalle herangezogen.

Résumé—Les auteurs ont étudié les réactions colorées de l'acide 2-quinizarine sulfonique (sel de sodium) et de l'acide 2-phénoxyquinizarine-3,4 disulfonique (sel de potassium) avec l'aluminium ou le béryllium et les ont comparées avec les variations de couleur acide-base normales. Les valeurs des pK de ces composés ont été déterminées par spectrophotométrie et comparées avec l'ionisation de l'acide 1,2-dihydroxyanthraquinone 3-sulfonique (sel de sodium). L'application des réactions colorées de l'acide 2-phénoxyquinizarine-3,4 disulfonique (sel de potassium) avec l'aluminium et le béryllium au dosage spectrophotométrique de ces deux ions métalliques est discutée.

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THE SPECTROPHOTOMETRIC DETERMINATION OF THE IONISATION CONSTANTS OF SOME DERIVATIVES OF BARBITURIC ACID

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Summary—The ionisation constants of dilituric acid (5-nitrobarbituric acid), violuric acid (5-isonitrosobarbituric acid) and 1,3-dimethylvioluric acid (1,3-dimethyl-5-isonitrosobarbituric acid) have been determined by measuring the variation of absorbance with pH. The spectrophotometric method offers a practical means of determining the dissociation constants of substances that ionise with a detectable change in their absorption spectra with change in pH.

INTRODUCTION

THE degree of dissociation of acid-base indicators has been determined by measuring the variation of absorbance with pH.[1] This method has been applied also to the determination of the ionisation constants of colourless acids whose ions absorb only in the ultraviolet region.[2] When absorbance is plotted as a function of pH for a series of solutions of the acid at constant concentration but varying pH, pK is equal to the pH at the point of maximum change of absorbance.

Solutions of violuric acid (5-isonitrosobarbituric acid) and 1,3-dimethylvioluric acid (1,3-dimethyl-5-isonitrosobarbituric acid) in water and in hexane are colourless in the visible region of the spectrum, but aqueous solutions of the alkali salts of the acids are coloured violet and absorb strongly at 540 mμ. Thus, it may be concluded that the undissociated acid does not absorb at 540 mμ but the dissociated acid does. This wavelength, then, can be used to measure the degree of ionisation of the acid. The dependence of absorbance on pH for 1,3-dimethylvioluric acid at 540 mμ is shown in Fig. 1.

In some cases this method can be used as a tool to determine the mechanism of a particular ionisation. Dilituric acid (5-nitrobarbituric acid) is too strong to allow its dissociation constant to be measured conductometrically.[3] Electrometric titrations indicate that the acid behaves like a strong monobasic acid with an acid strength between those of picric acid and hydrochloric acid.[4] It also has been described as a tribasic acid.[5] Most authors ascribe the yellow colour of aqueous solutions of salts of the acid to ionisation. This ionisation was investigated by following the change of absorption at 380 mμ with pH.

EXPERIMENTAL

Solutions of the acids

Violuric acid (Eastman Kodak Co.) was crystallised from distilled water and recrystallised from 95% ethanol yielding white crystals, m.p. 221–223° dec. (corr.).

1,3-*Dimethylvioluric acid* was synthesised by the condensation of 1,3-dimethylalloxan with hydroxylamine hydrochloride.[6] Crystallisation from 95% ethanol and drying at 110° yielded white crystals, m.p. 141–142°. (corr.).

1,3-*Dimethylalloxan* was prepared from caffein by the method of Biltz.[7]

Dilituric acid (Eastman Kodak Co.) was used as received, after drying at 110°.

* Present address: Boeing Airplane Co., Seattle 8, Washington, U.S.A.

Aqueous solutions of the various acids were prepared in distilled water. The molar concentrations of the solutions were as follows: violuric acid, $2{\cdot}97 \times 10^{-3}$; 1,3-dimethylvioluric acid, $4{\cdot}32 \times 10^{-3}$; and dilituric acid, $9{\cdot}75 \times 10^{-4}$.

Measurement of pH and absorbance

A Beckman Model G pH Meter was used to measure hydrogen ion concentration. The hydrogen ion concentrations of the solutions were increased by bubbling in carbon dioxide or by adding hydrochloric acid, with appropriate correction for dilution, which at no time exceeded 0·5%. To decrease

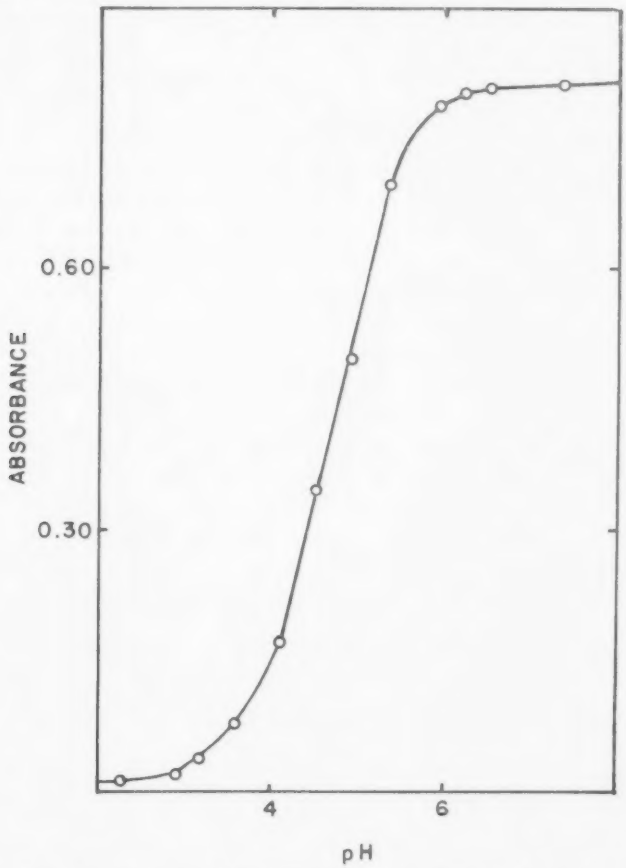

FIG. 1.—Dependence of colour formation upon pH in aqueous solutions of 1,3-dimethylvioluric acid at 540 mu.

the hydrogen ion concentrations, small increments of solid K_2CO_3 or concentrated KOH solution were added.

Absorbance measurements for violuric acid were made with a Beckman DU spectrophotometer at 504 mμ and 544 mμ and those for 1,3-dimethylvioluric acid were made at 540 mμ. Measurements for dilituric acid were at 380 mμ.

The dissociation constants of these acids were determined to be as follows: violuric acid, $K_1 = 3{\cdot}9 \times 10^{-5}$ and $K_2 = 2{\cdot}2 \times 10^{-10}$; 1,3-dimethylvioluric acid, $K_1 = 1{\cdot}9 \times 10^{-5}$; and dilituric acid $K_2 = 5{\cdot}6 \times 10^{-11}$.

RESULTS AND DISCUSSION

The monopotassium salt absorbs at 544 mμ and the dipotassium salt absorbs at 504 mμ; consequently the primary ionisation was measured at 544 mμ. The value

of $3{\cdot}9 \times 10^{-5}$ at 23° for the first ionisation constant for violuric acid compares favourably with $2{\cdot}7 \times 10^{-5}$ at 25° and $1{\cdot}992 \times 10^{-5}$ at 18°, found by other methods.[8,9] The secondary ionisation constant was measured at 504 mμ by measuring the increase in absorbance between pH 8 and 12 and was found to be $2{\cdot}2 \times 10^{-10}$. This probably represents the shift of a proton from position 1 to position 6, or equivalently from position 3 to position 4, with subsequent ionisation.

As the pH increased beyond 12, the absorbance at 504 mμ increased rapidly and that at 544 mμ decreased in a similar manner. Presumably these changes in absorption are due to the third possible ionisation.

The ionisation constant for 1,3-dimethylvioluric acid was $1{\cdot}9 \times 10^{-5}$ at 23°. It is thus a slightly weaker acid than violuric acid.

That the absorption by dilituric acid at 390 mμ—the absorption responsible for the yellow colour of the solutions—is due to ionisation only was inferred from the fact that the absorption obeys Beer's law. The effect of increasing pH is to increase the absorption from pH 8 to pH 13. The half-indicator colour occurred at pH 10·25; thus K_2 is $5{\cdot}6 \times 10^{-11}$ at 23°. This ionisation therefore is that of a very weak acid.

Another absorption band, attributable in part to ionisation, is affected only by a very high concentration of hydrogen ion. This absorption is probably due to the primary ionisation. The formation of the yellow colour results from a secondary ionisation of one of the hydrogens associated with a nitrogen at position 1 or 3 of the molecule. No other ionisation was detected, and it is believed that dilituric acid is a dibasic acid and that the yellow colour of solutions of salts of the acid is due to the second ionisation.

Good agreement was obtained with a known dissociation value for the first dissociation constant of violuric acid, although the spectrophotometric value was higher than that obtained by the conductivity method. The limiting factor controlling the accuracy of the determination is the pH measurement.

Zusammenfassung—Die Dissoziationskonstanten von Dilitursäure (5-Nitrobarbitursäure), Violursäure (5-Isonitrosobarbitursäure) und 1,3-Dimethylviolursäure wurden aus der pH-Abhängigkeit der Absorption berechnet. Die spectrophotometrische Methode ist gut geeignet um die Dissoziationskonstanten von Substanzen zu messen, die Änderungen der Absorptionsspektren mit dem pH zeigen.

Résumé—Les constantes de dissociation de l'acide diluturique (acide 5-nitrobarbiturique), de l'acide violurique (acide 5-isonitrosobarbiturique) et de l'acide 1,3-diméthylviolurique (acide 1,3-diméthyl-5-isonitrosobarbiturique) ont été déterminées par la mesure de leur variation d'absorption en fonction du pH. La spectrophotométrie est une méthode pratique pour la mesure de constantes de dissociation de substances qui s'ionisent en donnant des spectres d'absorption dont les variations en fonction du pH sont décelables.

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PHOTOMETRIC TITRATIONS—II

DESIGN AND CONSTRUCTION OF A PHOTOMETRIC TITRATOR

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Summary—The construction of a simple photometric titrator is described. The light receptor is a photo-diode whose design makes it easily possible to exclude external light. Consequently, titrations can be performed with the titration vessel in the open. Methods of treatment of results are discussed, and the possibilities of titrations according to the "ultimate precision method" are studied. The characteristics of the instrument are given, and tests of stability, sensitivity and linearity of response are dealt with. Some representative titration curves are presented.

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INTRODUCTION

IN the preceding paper of this series[1] it was pointed out that photometric end-point detection in chelometric titrations, without employing an indicator, is used less frequently than is warranted by its versatility. One of the reasons given was the underestimation of the possibilities offered by the method, partly because of a lack in development of the theoretical considerations. Another reason, the authors believe, is the limited availability of suitable instruments. For reasons previously discussed, automatic titrators* are excluded from consideration because they generally fail to respond appropriately in the most interesting cases, that is, where the system approaches certain limiting conditions such as very low stability constant of the metal chelate and/or extremely high dilution. Most examples of photometric titrators reported in the literature have been modifications of commercial filter photometers or spectrophotometers. The alterations are often difficult, and always limit the usefulness of an otherwise general-purpose instrument. The main disadvantage of a modified commercial instrument, and also of most of the more simply constructed titrators which have been described in the literature, however, is the basic requirement that the titration has to be performed in a light-tight compartment. This often leads to serious restrictions in the shape, and more importantly, in the size of the titration vessel. With a small sample, it is necessary to increase its volume so that all of the light beam passes through the solution. This, however, may lead to an excessive dilution, thus lessening the sensitivity of the method and favouring dissociation of the complex. On the other hand, if the volume of the sample is large, it may become necessary to use an aliquot portion, with the consequence that any error in the titration is multiplied by the aliquot ratio. A remedy which has been employed occasionally is to titrate outside the cuvette compartment, and to circulate the solution through the cuvette continuously by means of a pump. The disadvantages of this procedure are obvious. These and other possibilities have been considered in the literature. An extensive bibliography on the subject has been compiled recently by Headridge.[2]

Ideally, a photometric titrator should have the titration vessel directly in the light

* In order to avoid misunderstandings, an "automatic titrator" is defined as a device which shuts the burette off at the end-point. However, in order to titrate systems near the limiting conditions, it is necessary to obtain the whole titration curve, including the part beyond the equivalence point. Combining a titrator with an automatic burette and a strip-chart recorder allows one to obtain this curve automatically, but such an arrangement will not be considered as an automatic titrator.

beam of the instrument, while retaining the ability to operate in the open. The authors are aware of only two commercial instruments of this kind, but have not had the opportunity to examine either of them.[3,4]

It should be realised that the design requirements for a photometric titrator are in some respects much less stringent than those for a general purpose photometer. As will be shown later, it will in general suffice to read galvanometer scale divisions, because absolute values of transmittance or absorbance are not required for an end-point determination in photometric titrations. Positioning of the titration vessel in precisely the same way in successive titrations is unnecessary; it is, of course, mandatory to maintain the position of the titration vessel absolutely unchanged during any one titration. Further, the design characteristics of the titration vessel are not critical. In particular, the faces of the vessel need to be only approximately plane and parallel, and the exact length of the light path as well as the optical purity of the faces are of no moment.

It is, however, of utmost importance that the titrator possess high stability, at least over the period of a titration, because readjustment with a reference solution is in general impossible. (The reference solution may, for example, be the sample solution itself in its initial state).

In principle, there are two main possibilities for the operation of a photometric titrator with the titration vessel open to the ambient light. One is to use a very intense light source as the exciter lamp, and to moderate the intensity of the light just before it reaches the photocell by means of a grey wedge or a diaphragm. The effect of external light (*i.e.*, light from any source other than the exciter lamp) is thereby reduced by the same ratio. While the adverse effects of external light may be reduced in this manner to negligible proportions, two additional difficulties are introduced, namely, the production of large amounts of heat, and a decrease in stability of the light source because of its high power requirement.

The other possibility is to use modulated light which generates an alternating current signal in the detector circuit. External light in a properly designed apparatus will generate a signal which can be eliminated electronically. The more involved circuits, and the additional mechanical components (light chopper) required, may be considered to be somewhat disadvantageous.

In simple instruments, a low sensitivity microammeter is usually employed. Hence, a barrier-layer photocell is used in order to obtain an output capable of causing a full-scale deflection at the 100% transmittance setting. The characteristics of the common types of barrier-layer cells have been thoroughly reviewed elsewhere.[5]

Experimentation by the authors along this line showed that selenium cells could not be incorporated satisfactorily into the design of a photometric titrator. The low sensitivity per unit area, the fatigue effect and unfavourable spectral response of these cells mitigate against the prime requirement for a photometric titrator, namely, that of a relatively high order of stability.

After experimenting with a number of photocells and their associated electrical circuits, it was found that the Texas Instruments, Inc. type 1N2175 photo-duodiode is an eminently suitable light receptor. This quite inexpensive solid-state device consists of a symmetrically diffused NPN silicon junction mounted in the focal plane of a small lens. The entire device is only 12 mm in length and 2 mm in diameter; the photo-sensitive surface is only a fraction of 1 mm^2 in area. Sensitivity, as well as spectral

response characteristics, of the photo-diode was found to be very satisfactory for the present purpose. The greatest advantage which accrues from its use is the fact that in order to be focussed on the photosensitive area, light must reach the photo-cell lens within a certain angular range. Since the external light is almost entirely outside this range, its exclusion presents no difficulty.

The 1N2175 photo-diode, in conjunction with other well-known features of photometer design, led to the construction of a simple and inexpensive titrator described in the following sections.

THE PHOTOMETRIC TITRATOR

Design of instrument

The design of the instrument can readily be understood from Fig. 1. The light source (1) is a GE 425 lamp which draws about 0·75 amp from a 6-V lead accumulator. The lamp is placed at the focus

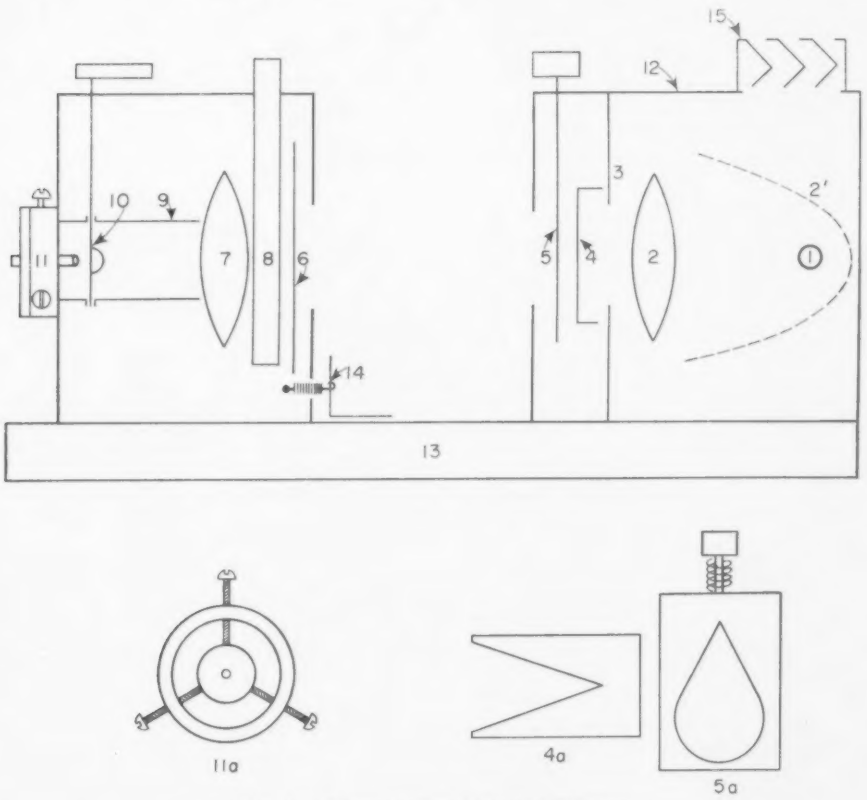

FIG. 1.—Schematic view of the phototitrator

1. Lamp, GE type 425
2. Condensing lens, 37·5 mm diam., F. L. 75 mm.
2′. Parabolic mirror
3. Circular diaphragm, 20 mm diam.
4. Adjustable wedge diaphragm, side view
4a. Adjustable wedge diaphragm, front view
5. Adjustable wedge diaphragm, side view
5a. Adjustable wedge diaphragm, front view
6. Self-closing shutter
7. Focussing lens, 37·5 mm diam., F. L. 75 mm.
8. Filter holder
9. 15 mm diam. tube
10. Zero adjusting shutter
11. Photocell and photocell mounting, side view
11a. Photocell and photocell mounting, front view
12. Lamp housing
13. Aluminium mounting angles.
14. Cell holder and springs
15. Chimney

of either a condensing lens (2) or a parabolic mirror (2′) to produce a nearly parallel light beam.

When the titrator is operated with a sufficiently sensitive galvanometer, *e.g.*, a Rubicon Instruments Co. instrument with a sensitivity of 7×10^{-10} amp/mm and a critical damping resistance factor of 47,000 ohms, the lamp may be operated below its rated power consumption. Hence, a rheostat has been placed in the lamp circuit (Fig. 4). This allows a rough regulation of the transmittance adjustment and increases the life of the lamp. If a less sensitive galvanometer is used, a different type of lamp with a higher power rating is required, and the rheostat in the lamp circuit may need to be changed.

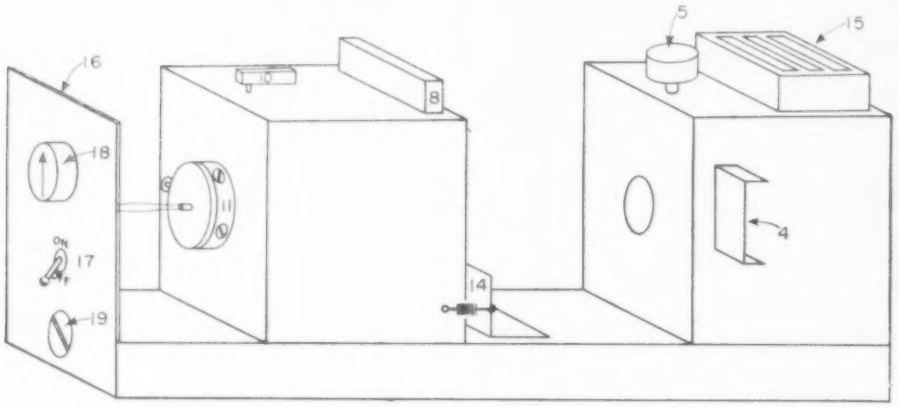

FIG. 2.—Perspective view of phototitrator

Numbers below 15 refer to same detail shown in Fig. 1

16. Panel
17 and 18. Switches
19. Battery holder

Optical adjustment of the light intensity is accomplished with two wedge diaphragms, the coarse adjustment by means of a sliding horizontal diaphragm (4, 4a) and the fine adjustment by means of a screw-driven vertical diaphragm (5, 5a) shown in Fig. 1. Ventilation of the lamp housing is secured by the provision of a chimney (12), but this is not essential to the satisfactory operation of the instrument when a low-energy lamp such as a GE 425 or similar type is used.

The exciter lamp compartment and the photocell compartment are about 15 cm apart, which distance permits utilisation of titration vessels of considerable size.

An aperture about 20 mm in diameter in the front plate of the photocell compartment limits the light beam sufficiently to ensure that only the most nearly parallel portion of it is utilised.

The filter holder, designed to accommodate filters of several thicknesses is shown in Fig. 3. Glass filters are suitable, but interference filters are preferable, having better monochromaticity and higher transmittancy. When the filter holder is removed from its position in the instrument, a weight operated shutter (6) closes automatically to prevent possible damage to the galvanometer if an intense beam of unfiltered light should strike the photocell.

Focussing the light on the photocell solely by adjustment of lens (8) is difficult, hence, to facilitate this operation, the photocell is placed in an adjustable mounting (11a). The fine adjustment can then be performed by turning the adjustment screws (with the receptor illuminated) until the maximum deflection of the galvanometer is obtained.

Effective exclusion of external light and stray light is accomplished by a tube (9) about 15 mm in diameter. Shutter (10) allows the photocell to be darkened completely when the zero point is adjusted on the galvanometer.

The exciter lamp compartment and photocell compartment are firmly mounted on two parallel pieces of 2·5 × 2·5 cm aluminium angle (13).

The titration vessel is held securely in its place by a spring clamp (14) which is made from a piece of aluminium angle at each end of which a small steel spring is attached. The other ends of the springs are in turn attached to opposite sides of the photocell compartment.

The entire apparatus is painted inside and out with a non-reflecting black lacquer. A perspective view of the photometer is shown in Fig. 2. The operation of the instrument needs no further explanation.

The electrical circuit

The electrical circuit is shown in Fig. 5; the characteristics of the components have been chosen to obtain the highest sensitivity of the instrument compatible with simplicity, ease of operation and

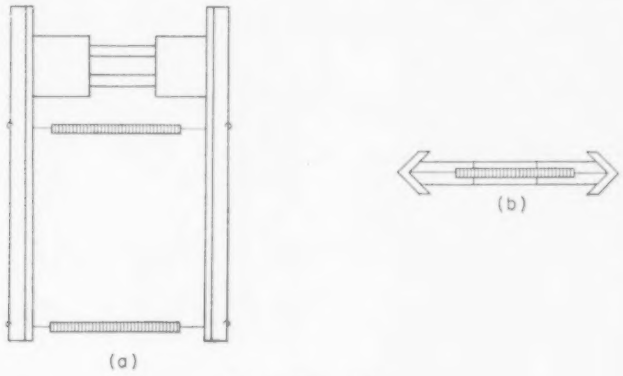

FIG. 3. Filter holder
(*a*) front view
(*b*) bottom view

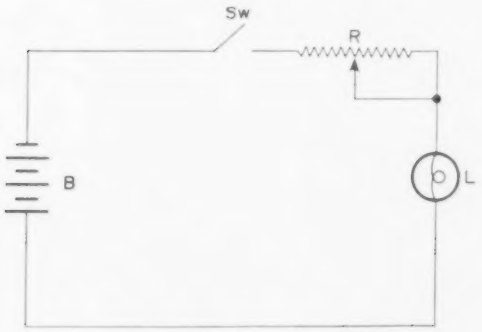

FIG. 4.—Lamp circuit
B Six volt lead accumulator
Sw SPST Switch
R 5-ohm, 10-watt rheostat
L Lamp, GE 425

appropriate stability. The photocell is a high-impedance device whose conductance is a linear function of light intensity over a wide range. It requires an external source of current which is provided by a TR 135 mercury battery rated at 6·5 v. Compensation for the dark current (approximately 0·01 μamp at 25°) is obtained by means of the zero-adjusting bridge circuit also shown in Fig. 5. The photocell is mounted co-axially in a cylindrical brass heat sink (see Figs. 1 and 2) to minimise drift of the dark current because of variation in temperature. Somewhat less than the critical damping of the galvanometer (the above mentioned Rubicon type) is provided by placing a 70,000-ohm resistor in a parallel circuit arrangement with the galvanometer and its zero-adjusting circuit. The resistance of the zero-adjusting circuit is approximately 500 ohms, and has a negligible effect on the damping of the galvanometer. Approximately 94% of the ultimate sensitivity of the galvanometer is

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utilised with this circuit. The switch (Sw2) allows the damping resistor to be removed from the circuit when, for example, the galvanometer is replaced by a strip-chart recorder for automatic recording of the titration curve (see footnote, p. 521). The use of shielded cable in all external wiring involving the photocell circuit was found to be essential to minimise spurious response by the galvanometer.

The switches (Sw1 and Sw2) and battery (B1) are mounted on a small panel behind the photocell compartment, and under the photocell compartment between the aluminium supports, respectively (see Fig. 2 and 5). This arrangement is advantageous in that it keeps the leads of the high-impedance part of the circuit as short as possible.

The zero adjustment circuit and the lamp rheostat, as well as their switches, are mounted in two separate panel boxes of appropriate size.

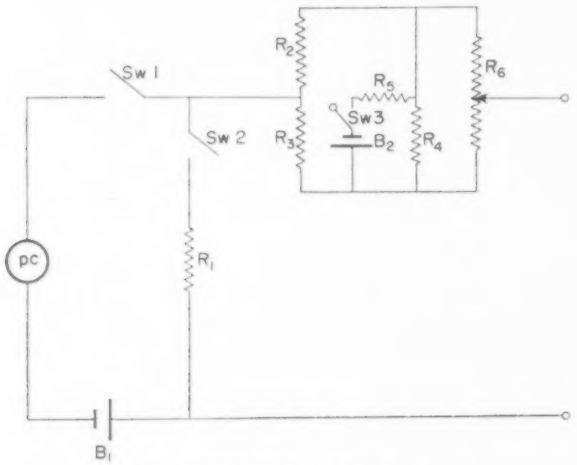

FIG. 5.—Electrical circuit for phototitrator

R_1 70,000 ohms
R_2 500 ohms
R_3 500 ohms
R_4 200,000 ohms
R_5 1·5 megohms
R_6 1000 ohms
B_1 TR 135 Mercury battery, 6·5 V
B_2 RM 640 Mercury cell, 1·35 V
PC Photocell, TI lN2175
Sw1, Sw2, Sw3, SPST switches

Operational characteristics

The instrument was subjected to tests to determine the linearity of its response, its stability and the effectiveness of the exclusion of external light.

Linearity of response of the photometer was determined by performing a number of titrations with systems under conditions known to give a linear change in absorbance with volume of titrant added and to have well-defined photometric end-points. The systems were copper^{II} with EDTA[6] in ammonia buffer at pH 10 and copper^{II} with triethylenetetramine[7] in acetate buffer at pH 7. An interference filter having its transmittance maximum at 620 mμ was used for both titrations. This is not the wavelength corresponding to the absorbance maximum of either system, but was the best choice from available filters. Examples of titration curves are represented in Fig. 6. It can readily be seen that the response of the instrument is linear, within the limits of experimental errors. The reproductibility of the end-points was within $\pm$0·02 ml, as can be expected in such titrations.

The overall stability of the photometer depends on the stability of the photocell dark current, of the light source, and of the electrical circuit.

The dark current arises from the conductance of the photocell at zero light intensity. The

important parameter for the stability of the instrument, however, is the sum of the dark current and the current in the zero-adjusting bridge circuit. The observed change of this current was approximately 5×10^{-10} amp per day. This variation corresponds to a drift of 0·5% T per day, which is negligible.

Stability of the light source was achieved by the use of an exciter lamp with low power requirement (less than 5 watts) in combination with a lead accumulator designed for continuous low-current drain.

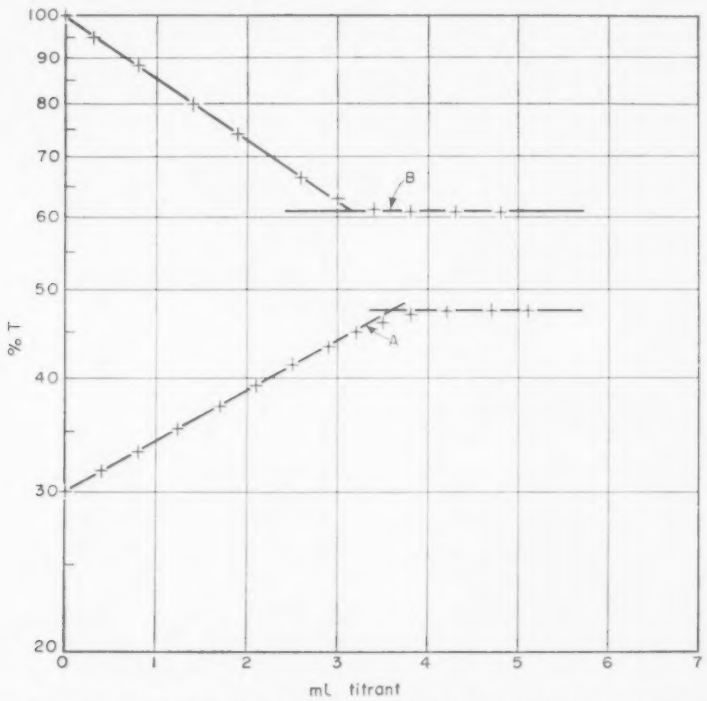

FIG. 6.—Titration of copper^{II} with EDTA at pH 10 (curve A), and triethylenetetramine at pH 7 (Curve B). (622 mμ)

This stabilised the light source sufficiently to keep the drift from a predetermined value below 0·1% T per hour.

Thus, the overall stability is very satisfactory.

The effectiveness of exclusion of external light was demonstrated by subjecting the apparatus to an intense beam of light from a 6-V flashlight or a 150-watt projection lamp. Even with the beam incident upon the aperture of the photocell compartment at an angle of about 30°, the smallest angle subtended by the lamp housing with respect to the aperture, no perceptible change in the galvanometer deflection occurred.

The titration vessel

As mentioned above, the focussing of the light beam on the small lens of the photocell is critical. Hence, the titration vessel must not deviate the light beam to a significant extent. High quality cuvettes are not essential, and vessels constructed in the following manner have proved to be entirely satisfactory.

Rectangular pieces of ordinary plate glass were cut to convenient sizes, and the surfaces to be joined were ground with abrasive material and bonded together with an epoxy resin. A number of cells with faces 10 × 10 cm and light paths of 1·5 to 5 cm have proved suitable for most macro titrations. Of course, any other size compatible with the dimensions of the photometer may be constructed when needed. For titrations to be performed at elevated temperature, analogous cells were made from

Pyrex plate glass. The increased temperature in such titrations was maintained by inserting a U-shaped Pyrex glass tube containing a small heating spiral.

Cells of these dimensions provide adequate space for insertion of a stirrer. The stirrer is a glass rod with a small propeller at the lower end, and is driven by a 6-V d.c. motor. It is important that direction of rotation and pitch of the propellor are such that the motion of the stirred liquid is from the bottom of the vessel towards the surface. This prevents formation of air bubbles which could seriously interfere with the titration.

TREATMENT OF RESULTS

One way to obtain the titration curve is to place the titration vessel filled with water (or the blank) in the light beam, to adjust the zero point with the shutter closed and then, with the shutter opened, to adjust 100% T with the diaphragms. The water (or blank) is then removed and the solution to be titrated is placed in the titration vessel. The galvanometer will indicate a transmittance between zero and 100% T. The titration is started, and the transmittance readings are recorded after the addition of each increment of titrant. Since the linear relationship is between absorbance, rather than transmittance, and the volume of titrant, the results may be treated in either of two ways.

Per cent T is transformed by the use of tables of logarithms into absorbance, and the latter is plotted on linear graph paper; or % T is plotted directly on semi-logarithmic paper. The latter is the simpler procedure.

However, the above procedure for setting zero and 100% T leads to a situation in which only a part of the galvanometer scale is used during the titration. Higher precision can be obtained by using a greater part of the scale (preferably the entire scale). It must be realised also that only 10 to 100% T can be plotted on one cycle semi-logarithmic paper.

Two cases may be distinguished when higher precision methods are used. An example will serve to elucidate the problem: Assume that the transmittance is adjusted to 100% T with water in the titration vessel, and when the sample is introduced the transmittance reads 50%. Further, assume that the transmittance decreases during the titration and reaches an ultimate value of 30%. Only 20 of the 100 scale divisions have been used. Assume now that the 100% T is adjusted with the starting solution instead of water, a process which can be achieved by operating the diaphragms so that the light intensity is increased. In this example the light intensity must be doubled; then, with regard to water as reference, the 100% T point is outside the galvanometer scale, *viz.*, at 200 S.D. (= scale divisions). In the titration performed with these adjustments, the scale range used will be from 100 S.D. to 60 S.D.

It is extremely important to note that the only difference in the plots of these two titration curves, on the same 1-cycle semi-logarithmic paper, is a parallel shift of one with respect to the other in the direction of the ordinate. The actual span on the ordinate is the same for each curve, because whatever the adjustment of the sensitivity of the galvanometer or light intensity, the fact remains that the absorbance change for the particular titration is unaffected by the method for plotting the results. In the example, the absorbance change, ΔA, is seen to be

$$\Delta A = -\log(0{\cdot}50) + \log(0{\cdot}20) = 0{\cdot}30 - 0{\cdot}70 = -0{\cdot}40,$$

which is the same ordinate distance on semi-logarithmic paper whether the plot is from 50 to 30 S.D. or from 100 to 60 S.D. In other words, the higher precision gained in the

galvanometer scale reading is nullified by the closer spacing of the lines on the graph paper.

In order to benefit from the increased precision in reading the galvanometer, it is necessary to convert transmittance readings into absorbance values, and to plot absorbance on a linear paper where it is at our disposal to select an appropriately higher precision scale.

The reverse case, that is, when the transmittance increases during the titration, is not handled as easily, as an example will show. Assume that the solution shows 50% T initially (100% T adjusted with water), and that during the titration the transmittance increases to 70%. Obviously, adjustment of 100% T with the starting solution will lead to the situation in which the galvanometer deflection will be outside the readable scale at some time during the titration. At first glance, the problem may seem to be solved with no difficulty by adjusting the 0% T electrically, with the starting solution as the zero reference instead of the closed shutter. This will give a titration curve which cannot be correct, as can be deduced from the following derivation.

In order to handle the problem in a completely general way, assume that the zero point is at M S.D. Adjustment of 100% T is performed, and N S.D. are read with the reference solution. When the sample is introduced into the light beam, the reading is P S.D. The % T corresponding to the reading P S.D., with respect to the total scale, is given by the relation

$$(N - M):100 = (P - M):\%\,\mathrm{T},$$

which yields

$$\%\,\mathrm{T} = 100\,(P - M)/(N - M).$$

Hence, the absorbance is given by

$$\mathrm{A} = -\log(\%\,\mathrm{T}/100) = -\log(P - M)/(N - M) = \log(N - M) - \log(P - M).$$

Returning to the first case, where $M = 0$, it can readily be seen that the absorbance is directly proportional to the logarithm of the reading P. As long as P is within the readable portion of the galvanometer scale, a plot of scale divisions on semi-logarithmic paper, or $-\log P$ (or even simply $+\log P$) on linear paper will yield a correct titration curve, displaced parallel to itself in the direction of the ordinate by an amount $\log N$. Since only the value of the abscissa at the end-point is wanted, this shift is unimportant.

In the second case, however, the zero-point is not at the galvanometer zero, that is, $M \neq 0$, and it is readily appreciated that the absorbance is now proportional to $\log(P - M)$. In order to plot the titration curve correctly, the value of M must be known. In practice this can be done by first setting the galvanometer zero with the shutter closed and then introducing the titration vessel containing the sample into the light beam. The galvanometer will now read M scale divisions, so that if the galvanometer is now readjusted to zero electrically, it is necessary to add the value M to each reading during the titration to obtain the correct curve. The electrical adjustment may be performed by applying an adjustable voltage to the terminals of the galvanometer to allow the entire scale to be shifted an arbitrary amount in either direction. To obtain higher precision, it is necessary to be able to adjust the sensitivity so that readings near the full-scale deflection are obtained at the end of the titration. However, adjustment of the 100% T with, for example, a pre-titrated sample having the same concentration as the sample to be determined, cannot be done after the shift of scale has been carried out,

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for this will change the value of M by an unknown factor. Nevertheless, it is possible both to determine the value of M and to utilise most of the scale with the following procedure: set the galvanometer zero in the usual way, then introduce a sample solution which has been titrated beyond the end-point, and open the shutter. Adjust the light intensity so that the galvanometer reads some convenient number of scale divisions not greater than $100 + M'$, where M' is an estimated value of M. (It is here assumed that the full-scale deflection of the galvanometer is 100 S.D.). It should be

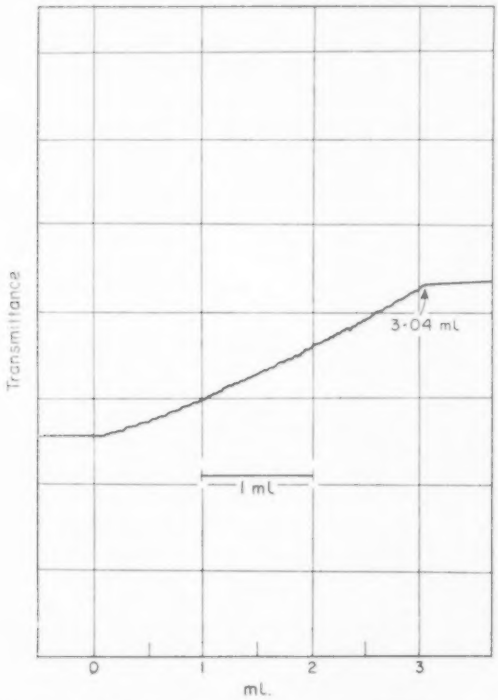

FIG. 7.—Automatic titration of copper^{II} with EDTA at pH 10 (649 mμ) using a Sargent Model C automatic burette and a Sargent Model MR recorder.
(Transmittance *vs.* ml titrant)

noted that M' is the estimated % T of the starting solution referred to the same solution, when the titration has been completed, as having 100% T. The solution in the titration vessel is replaced by a sample having the same initial concentration, whereupon the galvanometer will read between M' and 100. This readjusted value of M, must be added to each reading during the titration to obtain the correct curve. Application of an adjustable voltage to the terminals of the galvanometer can be used to re-set the galvanometer to zero. With this procedure, the galvanometer indicator will not leave the readable scale if $M' \leq M$ (original), and almost all of the scale will be used if M' and M are nearly equal.

Again, it should be pointed out that this procedure will not give higher precision when semi-logarithmic paper is used, and in order to benefit from this "ultimate precision" approach[8], it is necessary to convert the readings into absorbance values

and to plot these on linear paper with divisions selected to provide the appropriate precision.

Another possibility is to convert the output of the photocell circuit, which is proportional to transmittance, directly into absorbance readings by means of an electronic circuit. These circuits are rather involved and the range in which their output is a truly logarithmic function of the input is limited (see, *e.g.*, Ref. 9). Such an electronic conversion is of particular interest when the titration curve is plotted on a strip-chart recorder. It is, however, possible to plot the transmittance automatically, and in many cases the location of the end-point can be seen readily from the recorded curve. An example is shown in Fig. 7. For systems where the curvature is too great, and no sharp break is obtained, a useful procedure is to plot a number of points near the beginning and end of the recorded transmittance curve on semi-logarithmic paper, and to extrapolate in the usual way. This is much slower than having the absorbance recorded, but is less tedious than plotting the curve manually, point by point. In addition, it is advantageous to have the entire curve, and the method is especially suitable and time-saving in investigations to find the most suitable conditions when a new titration method is being developed.

Acknowledgements—Dr. T. S. Burkhalter, Texas Instruments, Inc., Dallas, Texas, provided a photodiode and took part in valuable discussions. The work was performed under a grant of the National Science Foundation. These aids are gratefully acknowledged.

Zusammenfassung—Die Konstruktion eines einfachen, photometrischen Titrationsgerätes wird beschrieben. Eine Photodiode wird als Lichtempfänger benützt, wodurch der Auschluss von Fremdlicht sehr leicht möglich ist. Das Titrationsgefäss kann daher auch während der Titration im offenen stehen. Methoden zur Auswertung der Daten werden behandelt und Möglichkeiten unter höchster Präzision zu arbeiten sind diskutiert. Die Charakteristiken des Instrumentes werden mitgeteilt und Ergebnisse der Prüfung von Stabilität, Empfindlichkeit und Linearität werden beschrieben. Einige typische Titrationskurven werden gezeigt.

Résumé—Les auteurs décrivent la construction d'un appareil simple de titrage photométrique. Le récepteur lumineux est un photomultiplicateur dont la conception permet d'exclure facilement la lumière extérieure. Par conséquent, les titrages peuvent être réalisés, le récipient étant à l'air libre. Les méthodes d'étude des résultats sont discutées, les possibilités de titrage en accord avec la "méthode de précision ultime" sont étudiées. Les auteurs donnent les caractéristiques de l'appareil, et discutent les tests de stabilité, de sensibilité et de linéarité de la réponse; ils donnent quelques courbes représentatives.

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IODOMETRIC DETERMINATION OF COPPER AND IRON IN ONE SOLUTION

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Summary—Copper^{II} and iron^{III} may be titrated iodometrically in a single solution. Copper is titrated first, iron being masked with fluoride. After the end-point is reached, aluminium chloride is added to de-mask the iron, which is titrated after some minutes. Good results are obtained.

INTRODUCTION

THE iodometric determination of copper^{II} in the presence of iron^{III} is usually performed in weakly acid medium. Iron is masked by fluoride. Just before the end-point, thiocyanate is often added, to liberate iodine, which is adsorbed on the CuI-precipitate. If no thiocyanate is added, low results are obtained.[1] The reaction between iron^{III} and iodide is performed at pH ~1. The reaction is rather slow, therefore 15–30 minutes should be allowed before titrating. Alternatively some CuI suspension may be added as a catalyst, when the titration may be performed immediately.

Two papers[2,3] are known to the present authors, dealing with the iodometric titration of both ions in the same solution. In both papers iron is masked with fluoride. After the copper end-point is reached, the solution is acidified, and boric acid is added to de-mask the iron. The iron is titrated as described above. In the first paper, that of Lang and Reifer,[2] two points should be noted: (1) no thiocyanate was added, and (2) if small quantities of copper were present, not enough CuI was formed for the catalytic action. Therefore a known amount of copper was added before the titration.

The second paper by Kinnunen and Wennerstrand,[3] deals with the analysis of copper-base alloys, in which the iron-content is low. It is stressed that no thiocyanate should be used in the copper titration if iron is to be determined afterwards.

In both methods large amounts of ammonium salts are present before the titration begins. In the first, 5–10 g of $(NH_4)_2SO_4$ are added; in the second the excess of HNO_3, used to dissolve the alloy, is neutralised with NH_4OH.

EXPERIMENTAL

The use of boric acid as demasking agent

The experiments of Lang and Reifer[2] were repeated. About 1 mmole of copper and 1·2 mmole of iron were present. It was found, however, that poor results were obtained for iron unless, after dissolution of the boric acid, the titration of iron was delayed for about 1 hr. Presumably this time is necessary for complete de-masking of the iron.

Several changes in the experimental conditions were tried to accelerate the de-masking reaction. They included addition of thiocyanate at several stages of the procedure, replacement of ammonium sulphate by other salts, or omission of this salt (sulphate ion has been reported to slow down the reaction between iron^{III} and iodide[4]). However, no improvement was found.

In an attempt to reproduce the work of Kinnunen and Wennerstrand,[3] some experiments were performed in which the quantity of iron was about 0·25 mmole. Results for copper were slightly low, because no thiocyanate was used. For iron, results were satisfactory, though it was necessary

to wait a few minutes after boric acid was added, before the iron titration was started. For larger amounts of iron, however, poor results were obtained with this procedure.

Another de-masking agent was therefore sought. The stability constants compiled by Bjerrum *et al.*[5] showed that the use of aluminium and thorium might lead to success. Aluminium was selected for further investigation.

TABLE I.—TITRATION OF COPPER-IRON MIXTURES
(Second series of experiments)

No. of experiment	0·1*N* thiosulphate, for copper, *ml*			0·1*N* thiosulphate, for iron, *ml*		
	used	calc.	diff.	used	calc.	diff.
1	6·42	6·43	+0·01	31·20	31·21	−0·01
2	6·43	6·43	0·00	31·27	31·21	+0·07
3	12·90	12·94	−0·04	26·02	26·03	−0·01
4	12·93	12·94	−0·01	26·00	26·03	−0·03
5	19·40	19·37	+0·03	20·80	20·82	−0·02
6	19·39	19·37	+0·02	20·84	20·82	+0·02
7	25·90	25·88	−0·02	15·55	15·59	−0·04
8	25·87	25·88	−0,01	15·59	15·59	0·00
9	32·31	32·33	−0·02	10·50	10·41	+0·09
10	32·33	32·33	0·00	10·42	10·41	+0·01
11	38·75	38·76	−0·01	5·24	5·18	+0·06
12	38·77	38·76	+0·01	5·24	5·18	+0·06
	Mean difference: 0·00 ml			Mean difference: +0·017 ml		

The use of aluminium as a demasking agent

Stock solutions of copper^{II} and iron^{III} were prepared by dissolving pure copper in nitric acid and by dissolving iron^{III} oxide p.a. in hydrochloric acid. The concentrations were checked iodometrically and (for copper only) electrolytically, and were 268·93 mg of copper and 150·8 mg of iron^{III} oxide in 25 ml of stock solution.

Procedure: Twenty-five ml of each of the stock-solutions were transferred to a flask, and neutralised with NH_4OH; 800 mg of KHF_2 were added, and, after the precipitate had dissolved, 2–3 g of KI. The titration was performed with 0·1*N* thiosulphate solution, standardised with KIO_3. After the starch end-point was reached, 10 ml of 10% KCNS solution were added and the titration was completed. Then 25 ml of a solution of $AlCl_3$, containing 2·2 g of Al, were added. There was sufficient free HCl in the $AlCl_3$ solution to give pH ~1. Some $NaHCO_3$ was added to eliminate the influence of oxygen, and the mixture was shaken for some min and titrated again with thiosulphate solution.

For copper, from seven experiments, the mean value, standard deviation and confidence limits ($\alpha = 0{\cdot}05$) were found to be 269·04 mg, 0·06% (= 0·16 mg) and 268·89–269·18 mg. For iron these values were 150·5 mg, 0·2% (= 0·3 mg) and 150·2–150·8 mg.

A second series of experiments was performed in order to investigate the influence of the amounts of copper and iron present on the accuracy of the analysis. Some differences in the conditions, which are not believed to have affected the results, were: (1) NH_4HF was used instead of KHF_2. (2) Because in some of the experiments much more iron was present than in the first series, 2 g of the masking agent were added. (3) 40 ml of an $AlCl_3$ solution containing 1·6 g of Al were used, and as this solution was only weakly acid, 10 ml of 5*N* H_2SO_4 were added. (4) The iron solution was prepared from $Fe(NO_3)_3$ and standardised against thiosulphate. (5) The amount of NH_4OH necessary to neutralise the copper-iron solution varied with the amount of the metals; the NH_4-solution was added until the blue colour of the copper-ammine complex was just formed. Results of the second series of experiments are given in Table I.

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DISCUSSION

As might be expected, results for copper are very good in both series of experiments. For iron, the results in the first series seem quite good, although there may be a slight systematic negative error.

The results in the second series seem slightly too high for small quantities of iron. This was confirmed by duplicating experiments 11 and 12. These results, were slightly too high by 0·04 and 0·06 ml respectively. A blank value of 0·02–0·03 ml was found in some experiments, giving a partial explanation of the high results. No further investigations were carried out to eliminate the discrepancy.

From all the experiments, it may be concluded that results for copper are very good. For large amounts of iron, results are good. For small amounts of iron the results seem slightly high, but the error is not more than about 0·5% if a blank is subtracted.

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Zusammenfassung—Kupfer(II) und Eisen(III) werden hintereinander in einer Lösung jodometrisch titriert. Bei der Kupfertitration wird Eisen mit Fluorid maskiert. Nachdem wird Eisen mit Aluminium demaskiert und nach einigen Minuten ebenfalls jodometrisch titriert. Die Ergebnisse sind gut.

Résumé—Le cuivre(II) et le fer(III) sont titrés l'un après l'autre dans une seule solution. D'abord on ajoute du iodure et du fluorure et en milieu peu acide le fer est masqué par le fluoride et le iode, libéré par la réaction avec le cuivre, et titré avec le thiosulphate. Après le titrage on ajoute de l'aluminium pour libérer le fer de son complex fluoride, et après quelques minutes le titrage du fer est effectué en milieu acide par le thiosulphate. Les résultats sont bons.

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ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—III

HIGHLY SELECTIVE DETERMINATION OF TRACE AMOUNTS OF MERCURY

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Summary—Mercury has been determined by dithizone in amounts of 10^{-6} to 10^{-7} g/ml with an average precision of $\pm 0{\cdot}5\%$ and in amounts of 10^{-8} to 10^{-9} g/ml with an average precision of $\pm 2{\cdot}5\%$. The determination of smaller amounts of mercury was subject to larger errors because of the lower specific activity of the radio-mercury employed. In the analysis even a significant excess of metals which also form extractable complexes with dithizone does not interfere. The method is very rapid and simple, because it consists of a single extraction of the analysed solution, and measurement of the activity of the extract. The procedure which has been worked out is far more precise and sensitive than the colorimetric determination of mercury by dithizone or other organic agents.

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INTRODUCTION

THE method described in this paper is based on variation in the initial specific activity of a tracer, as a result of dilution with the inactive element under investigation. In the first paper[1] of this series the theoretical basis for isotopic dilution analysis by extraction was laid down. From this the conditions for the determination of a number of elements may be derived. As has been shown,[1] this method can be used for the analysis of trace amounts of an element, by always extracting the same amount of this element from solutions of different concentrations. This may be done by using a smaller amount of the organic reagent forming the extractable complex than would correspond stoichiometrically to the amount of the element present.

On this basis a highly selective determination of trace amounts of zinc has been worked out.[2] In this paper the determination of mercury is described in conditions previously predicted. In the determination of trace amounts of zinc, selectivity was achieved by using the precipitating reagent, diethanoldithiocarbamate. In determining mercury by dithizone the presence of a masking agent is not, however, necessary, since the value of the equilibrium constant for the extraction of mercury dithizonate is so high that even a large excess of other metals forming extractable dithizonate complexes does not interfere in the determination.

EXPERIMENTAL

Apparatus

A scintillation counter with a well-type NaI[Tl] crystal. A mechanical shaker. Glass test-tubes of 25-ml volume, with ground stoppers.

Chemicals

Water: Redistilled
Carbon tetrachloride: A.R., redistilled.
Dithizone: A.R.

Sulphuric acid: A.R., 50% and 5% solutions, purified by extraction with a CCl_4-dithizone solution.

Radiomercury solution: (^{203}Hg . $T_{1/2}$ = 46·5 days). The solution of specific activity 30 mC/g was always diluted to the appropriate concentration using 5% H_2SO_4 solution.

Non-active mercury solution: This was prepared by dissolving redistilled metal of A.R. purity in A.R. HNO_3 and diluting to the required concentration using 5% H_2SO_4 solution.

Procedure

To 10 ml of the solution of non-active mercury (10^{-6} to 10^{-7} g/ml), containing a large excess of other metals (see Table I), an amount, of the same order of magnitude, of radiomercury is added. To this solution 4 ml of 50% H_2SO_4 and 1 ml of 10% $NH_2OH{\cdot}HCl$ are added. (Hydroxylamine is added in order to reduce oxidising agents, which may be present, and which would decompose dithizone.) The solution thus prepared is extracted by 1·5 ml of 2×10^{-5} *M* dithizone solution in CCl_4. After shaking for 10–20 min (this time is sufficient to reach equilibrium) the organic phase is separated, and the activity of 1·00 ml of the extract is measured by the scintillation counter (A_2). At the same time, a solution which contains only radiomercury, 4 ml of 50% H_2SO_4 solution, 1 ml of 10% $NH_2OH{\cdot}HCl$ solution and about 1·5 ml of the dithizone solution, is extracted. The activity of 1·00 ml of this extract is measured in the same way (A_1).

The amount of non-active mercury is determined from the relation:

$$x = y \cdot \left[\frac{A_1}{A_2} - 1\right]$$

In determining smaller amounts of mercury the same procedure is followed, again adding amounts of radiomercury of the same order of magnitude (the most satisfactory ratio of active and non-active mercury is 1:1) and less dithizone than corresponds to the amount of mercury present (see c_{HA}, Table I). Because a more dilute solution of dithizone is used, the solution to be analysed should be less acid; therefore a smaller amount of sulphuric acid (4 ml of 5% H_2SO_4 solution) is added.

RESULTS AND DISCUSSION

The results show that the method can be used to determine amounts of 3×10^{-6}–3×10^{-7} g/ml with an average precision of ±0·5%, and amounts of 3×10^{-8}–3×10^{-9} g/ml with an average precision of ±2·5%. The determination of amounts of mercury larger than 10^{-6} g/ml is not satisfactory, because in this concentration range colorimetric determination can be carried out with good precision. In determining amounts of mercury of 10^{-10} g/ml the errors of the determination are higher (see Table I). The reason for this was the low specific activity of the radiomercury employed. As a result of this, the measured activity was approximately the same as the background of the counter. If, however, radiomercury of higher specific activity or carrier-free mercury were used, it would be possible to determine with sufficient precision mercury concentrations which were lower by an order of magnitude.

From Table I it follows that the results obtained are not only precise but also accurate. This is to be seen from low values of the difference $\sigma - X$

where $$\sigma = \frac{\sum_{x=1}^{x=n} x}{n}$$

and X is the amount of mercury taken for analysis.

All stock solutions of active and non-active mercury must contain sufficient sulphuric acid (an approximately 5% solution) to eliminate hydrolysis and adsorption on the walls of vessels.

In this determination even a large excess of metals forming extractable complexes with dithizone does not interfere. Nor is the result of the determination influenced by

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the presence of insoluble chlorides and sulphates of the metals listed. The presence of Sn^{2+} interferes in the determination by reducing mercury to the metallic state.

In agreement with theory,[1] it has been found that variation of the sulphuric acid concentration in the range 1–20% does not influence the extraction of mercury by dithizone.

TABLE 1.—EXTRACTION OF MERCURY BY DITHIZONE

($2{\cdot}7 \times 10^{-7}$ g Hg/ml–$5{\cdot}6 \times 10^{-10}$ g Hg/ml[a])

Mercury taken, μg (X)	Active mercury added, μg (y)	Activity of extracts[b] (A_1)	Activity of extracts[b] (A_2)	Mercury found, μg (x)	Deviation from means, μg (Δ)	Other metals present, μg	Deviations
2·783	1·739	71·644	27·222	2·838	+0·058	1000 Cd	
		71·644	27·195	2·843	+0·063	1000 Co	
		71·644	27·790	2·745	−0·035	1000 Cu	
		71·644	27·780	2·746	−0·034	1000 Fe	$\sigma = 2{\cdot}780$
		71·644	27·440	2·802	+0·022	1000 Mn	$\delta = \pm 0{\cdot}0137 = \pm 0{\cdot}5\%$
		71·644	27·683	2·762	−0·018	1000 Pb	$\sigma - X = -0{\cdot}003 = -1{\cdot}1\%$
		71·644	27·666	2·765	−0·015	1000 Tl	
		71·644	27·910	2·728	−0·052	1000 Zn	
		71·644	27·503	2·791	+0·011	1000 Ag	
0·2783	0·3478	15·600	9·020	0·2537	−0·0313	100 Cu	
		15·600	9·138	0·2460	−0·0390	100 Co	
		17·241	9·661	0·2729	−0·0121	100 Cd	
		17·241	9·513	0·2826	−0·0024	100 Fe	$\sigma = 0{\cdot}2850$
		17·241	9·272	0·2988	+0·0138	100 Mn	$\delta = \pm 0{\cdot}0086 = \pm 3{\cdot}0\%$
		17·241	9·165	0·3062	+0·0212	100 Pb	$\sigma - X = +0{\cdot}0067 = +2{\cdot}4\%$
		17·241	8·999	0·3136	+0·0286	100 Zn	
		17·241	9·169	0·3062	+0·0212	100 Bi	
0·02783	0·06957	3·255	2·290	0·02931	+0·00204	50 Cd	
		3·500	2·460	0·02941	+0·00214	50 Cu	
		3·500	2·500	0·02783	+0·00056	50 Pb	
		3·500	2·529	0·02671	−0·00056	50 Tl	$\sigma = 0{\cdot}02727$
		3·500	2·580	0·02500	−0·00227	50 Zn	$\delta = \pm 0{\cdot}00055 = \pm 2{\cdot}0\%$
		3·500	2·574	0·02500	−0·00227	50 Mn	$\sigma - X = -0{\cdot}00056 = -2{\cdot}0\%$
		2·393	1·715	0·02750	+0·00023	50 Fe	
		2·393	1·700	0·02830	+0·00103	50 Ce	
		2·393	1·735	0·02640	−0·00087	50 Ni	
0·0056	0·0695	3·500	3·110	0·0087			$\sigma = 0{\cdot}0094$
		2·393	2·090	0·0102			$\sigma - X = +0{\cdot}0038 = +67\%$

[a] Volume of solution analysed in all experiments listed in Table was 10 ml.

[b] In the range $2{\cdot}7 \times 10^{-7}$ g Hg/ml $c_{HA} = 2{\cdot}10^{-5}M$ and A_1, A_2, are expressed in counts/2 min.
In the range $2{\cdot}7 \times 10^{-8}$ g Hg/ml $c_{HA} = 2{\cdot}10^{-6}M$ and A_1, A_2, are expressed in counts/5 min.
In the range $2{\cdot}7 \times 10^{-9}$ g Hg/ml $c_{HA} = 4{\cdot}10^{-7}M$ and A_1, A_2, are expressed in counts/5 min.
In the range $5{\cdot}6 \times 10^{-10}$ g Hg/ml $c_{Ha} = 4{\cdot}10^{-7}M$ and A_1, A_2, are expressed in counts/5 min.

All activities listed in table are mean values for three measurements.

[c] $\sigma = \dfrac{\sum_{x=1}^{x=n} x}{n}$. $\quad \delta = \pm\sqrt{\dfrac{\Sigma\Delta^2}{n(n-1)}}$.

The proposed method is very simple and rapid. A single extraction of mercury from a solution containing an excess of interfering metals is far more simple than the conventional determination of mercury by dithizone. Comparison of our results with data from the literature[3] indicates that the determination of mercury by this method is more sensitive (maximum sensitivities of the methods mentioned are given in brackets) than determination by flame photometry (10^{-4} g/ml), by the graphite DC arc (2×10^{-6} g/ml), by the copper spark (5×10^{-6} g/ml), colorimetrically (8×10^{-8} g/ml) or by activation analysis (neutron flux, 10^{13} neutrons cm^2 sec, $6{\cdot}5 \times 10^{-9}$ g/ml). In comparison with activation analysis, the proposed method has the further advantage that less complicated instruments are required, and the activity handled is negligible. In activation analysis it is often necessary to work with high radio-isotope activities, arising from other elements also present in the irradiated sample.

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CONCLUSION

In the present paper a highly selective method for the determination of trace amounts of mercury, of the order of 10^{-6}–10^{-10} g Hg/ml, is described. The determination is carried out by the method of isotopic dilution analysis using solvent extraction. The method should be suitable for the determination of mercury in various materials, and its sensitivity might be further increased by using carrier-free radiomercury.

Zusammenfassung—Quecksilber in Mengen von 10^{-6}–10^{-7} g/ml können mittels Dithizon mit einer mittleren Genauigkeit von $\pm 0.5\%$ bestimmt werden. Für zehnfach geringere Mengen liegt die Genauigkeit bei $\pm 2{,}5\%$. Die Bestimmung noch kleinerer Mengen war mit grösseren Fehlern behaftet, was auf die niedere spezifische Aktivität des Radioquecksilbers zurückzuführen ist. Die Analyse wird selbst durch beträchtliche Mengen anderer Metalle, die ebenfalls Dithizonkomplexe formen, nicht gestört. Die Methode ist rasch und einfach und besteht aus einer einzigen Extraktion mit anschliessender Messung der Radioaktivität des Extraktes. Die Methode is empfindlicher und genauer als die Bestimmung des Quecksilbers mit Dithizon oder anderen organischen Reagenzien auf photometrischem Wege.

Résumé—Les auteurs ont dosé le mercure par la dithizone: en quantités de 10^{-6}–10^{-7} g/ml avec une précision moyenne de $\pm 0{,}5$ pour cent, en quantités de 10^{-8}–10^{-9} g/ml avec une précision de $\pm 2{,}5$ pour cent. Le dosage de plus faibles quantités de mercure est sujet à une plus grande erreur à cause de la plus faible activité spécifique du radiomercure employé.

Des quantités même importantes de métaux qui forment des complexes extractibles par la dithizone ne gênent pas dans l'analyse. La méthode est très rapide et simple, car elle consiste en une extraction de la solution à analyser, puis en une mesure de l'activité du composé extrait. Ce procédé est beaucoup plus précis et sensible que le dosage colorimétrique du mercure par la dithizone ou d'autres réactifs organiques.

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TITRIMETRIC DETERMINATION OF INDIGO SULPHONATE WITH POTASSIUM IODATE

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Summary—Conditions have been established for the direct titration of indigo sulphonate with potassium iodate at room temperature. The titration can be carried out in a medium which is 6–8*N* with respect to hydrochloric acid. The blue colour of the indigo disappears sharply at the end-point, giving a clear yellow solution. It has been observed that 1 g mole of indigo consumes very nearly 1 g mole of potassium iodate. The reaction of indigo sulphonate with potassium iodate is very slow, but is markedly accelerated by chloride ion. Direct titration of indigo sulphonate has also been found possible in mixed acid media containing sulphuric and hydrochloric acids at suitable concentrations. The stoichiometry observed in these titrations is in striking contrast with the reported deviations in the titrations of indigo sulphonate with potassium permanganate and cerium^{IV} sulphate. Evidence has also been obtained for the formation of a new type of iodo derivative of isatin sulphonate in the reaction between indigo sulphonate and potassium iodate. The new iodo-isatin sulphonate is capable of liberating iodine from potassium iodide quantitatively.

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THE determination of indigo has received considerable attention in view of its commercial importance. Potassium permanganate has been employed for its oxidimetric determination after conversion of the indigo to the soluble indigo sulphonic acid, by Rawson,[1] Bergtheil and Briggs,[2] Bloxam,[3] Heinisch,[4] Thomson,[5] Wagner[6] and others.

It is usually believed that in this titration the blue indigo sulphonic acid is oxidised to yellow isatin sulphonic acid. Although the amount of potassium permanganate consumed in this titration is less than that required by the stoichiometric equation, the method has still been widely adopted in view of its great convenience. A dilute solution of indigo sulphonic acid can be rapidly titrated, at room temperature, with a dilute solution of potassium permanganate, the colour change from blue (of the indigo) to yellow (of the isatin) being sharp. Allen[7] suggested that a fairly accurate assay could be made by carrying out the titration under a prescribed set of conditions and applying a correction factor. Gopala Rao, Venkateswara Rao and Subramanyam[8] investigated the use of cerium^{IV} sulphate for the titration of indigo sulphonic acid. They observed that the reaction is very fast, making a direct titration feasible; the amount of cerium^{IV} sulphate required, however, is less than that required by the equation representing the oxidation of indigo sulphonic acid to isatin sulphonic acid. Nevertheless, these investigators found that if the titration of indigo sulphonic acid is carried out at a concentration of about 0·002*N* with a 0·02*N* cerium^{IV} sulphate solution, in 0·5*N* to 2·0*N* sulphuric acid, the correct assay of indigo could be made by multiplying the experimental value by a correction factor which has an average value of 1·16 under the conditions.

Narasimha Sastri and Gopala Rao[9] found that, in the presence of oxalic acid acting as a catalyst, indigo sulphonic acid is rapidly oxidised by sodium metavanadate when present in excess. Although this reaction forms the basis of an indirect method of determination, the method is of great value in view of the fact that the reaction is

stoichiometric. Gopala Rao and Venkateswara Rao[10] studied the oxidation of indigo sulphonic acid by excess potassium dichromate in a sulphuric acid medium. It was observed that the oxidation with 0·025*N* potassium dichromate proceeds stoichiometrically when the sulphuric acid concentration is below 0·7*N*. Under these conditions, they found that the assay of indigo could be carried out with great accuracy.

We have investigated the use of potassium iodate as an oxidimetric reagent for the determination of indigo sulphonate. Indigo sulphonate is only very slowly oxidised by an excess of potassium iodate in a sulphuric acid medium, but the reaction is quite rapid in a hydrochloric acid medium. In a 0·5*N* hydrochloric acid medium, it can be completely oxidised to isatin sulphonate in about 40 min when treated with an excess of potassium iodate at room temperature. In the process, 1 g mole of indigo sulphonate consumes very nearly 2/3 g mole of potassium iodate. This reaction has been utilised for the determination of indigo carmine as follows:

An aliquot of the indigo sulphonate solution is allowed to react in 0·5*N* hydrochloric acid with a known excess of standard potassium iodate solution until the blue colour of the indigo gives place to the clear yellow of isatin. The mixture is then treated with an excess of potassium iodide, which interacts with the unreacted potassium iodate giving iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulphate, using starch solution as indicator. In this way, the amount of potassium iodate that has reacted with the indigo sulphonate is calculated.

Details of this method have been presented at the Analytical Congress (1961) organised by the Hungarian Chemical Society. Continuing the work on the same reaction, we have now been able to establish conditions for the direct titration of indigo carmine with a standard solution of potassium iodate at room temperature. The details of this investigation are presented below.

EXPERIMENTAL

Reagents

Indigo: A sample of pure synthetic indigo is sulphonated and standardised by the methods already described.[7–9]

Potassium iodate: An approximately 0·05*N* or 0·02*N* solution is prepared from "Baker's Analyzed" C.P. Sample and standardised according the following procedure: 20 ml of 1:4 hydrochloric acid solution is added to 10 ml of a 10% potassium iodide solution contained in a 250-ml iodine flask. Ten ml of the potassium iodate solution are pipetted into this mixture and the flask is stoppered. The sides of the flask are washed with water, and the total volume is made up to 100 ml by adding distilled water. The liberated iodine is titrated with a standard sodium thiosulphate solution which has been standardised against standard potassium dichromate solution, using starch solution as indicator.

The other reagents are of analytical grade.

RESULTS AND DISCUSSION

Direct Titration of Indigo Carmine with Potassium Iodate in a Hydrochloric Acid Medium

An extended investigation of the influence of hydrochloric acid concentration on the indigo-iodate reaction has revealed that an increase in the hydrochloric acid concentration retards the reaction up to a certain limit, beyond which there is an acceleration. The results are given in Table I.

This interesting observation has been utilised for the direct titration of indigo carmine with potassium iodate. We have found that it is possible to carry out the titration in a medium which will be at least 6*N* with respect to hydrochloric acid at the

end of the titration. The blue colour of the indigo disappears sharply at the end-point giving place to a clear yellow colour. The titration can be carried out at normal speed without any difficulty. Very nearly 1 mole of potassium iodate is required for each mole of indigo. The results are summarised in Table II. Similar results have been obtained in titrations conducted in 7*N* and 8*N* hydrochloric acid.

TABLE I. 3 ML OF INDIGO SULPHONATE (ABOUT $7{\cdot}0 \times 10^{-3}M$) + X ML OF CONCENTRATED HYDROCHLORIC ACID TO MAKE UP THE REQUIRED OVERALL ACIDITY + 10 ML OF 0·02177*N* POTASSIUM IODATE + WATER TO MAKE UP TO 50 ML; *temperature* 28°.

Overall normality of hydrochloric acid, *N*	Time taken for complete oxidation of indigo
0·1	23 min
0·2	25 min
0·3	30 min
0·4	35 min
0·5	40 min
1·0	55 min
1·5	75 min
2·0	90 min
2·5	65 min
3·0	28 min
4·0	30 sec
5·0	15 sec
6·0	5 sec
7·0	Instantaneous
8·0	Instantaneous

TABLE II. X ML OF INDIGO SULPHONATE + Y ML OF CONCENTRATED HYDROCHLORIC ACID TO MAKE UP TO 6*N* AT THE END OF THE TITRATION + WATER TO MAKE UP TO 50 ML. TITRATED WITH $8{\cdot}882 \times 10^{-3}M$ OR 0·05330*N* POTASSIUM IODATE SOLUTION.

Indigo taken, *millimoles*	Potassium iodate consumed, *millimoles*	Moles of iodate / Moles of indigo
0·02231	0·02256	1·011
0·02975	0·02984	1·003
0·03718	0·03713	0·998
0·04463	0·04423	0·991
0·05206	0·05116	0·983
0·05950	0·05861	0·985
		Average 0·995

A large number of determinations of indigo carmine have been made according to this direct procedure. The results given in Table II show that the determination of indigo can be made very easily with an accuracy of 0·2–1·7%.

When indigo carmine is treated with an excess of potassium iodate in 0·5*N* hydrochloric acid, the number of moles of potassium iodate consumed per mole of indigo is

0·619 (nearly 2/3). In the direct titrations carried out at a high hydrochloric acid concentration, the mole ratio is very nearly 1:1. In trying to reconcile the two sets of experiments, it was observed that the titration mixture (left after the direct titration) contains a compound which is capable of liberating iodine from potassium iodide. While the titration mixture itself does not give a blue colour with starch, it does so after the addition of a drop or two of potassium iodide. The amount of the oxidising substance formed during a direct titration was determined quantitatively.

The residual titration mixture was suitably diluted so that the acid concentration fell from 6*N* to 1*N* and was then treated with a slight excess of potassium iodide. After keeping for 1–2 min, the mixture was titrated with a standard solution of sodium thiosulphate, using starch as indicator. The dilution prescribed is necessary because a high concentration of acid vitiates the titration with sodium thiosulphate.

The results given in Table III show that the oxygen equivalent of 1/3 of the potassium iodate consumed in the titration is recoverable in the manner indicated above.

TABLE III

Indigo taken, *millimoles*	Iodate consumed, *millimoles*	New oxidising substance formed in terms of potassium iodate, *moles*
0·02249	0·02292	0·00760
0·02999	0·03038	0·01009
0·03749	0·03819	0·01268
0·04499	0·04547	0·01512
0·05248	0·05330	0·01771
0·05998	0·06092	0·02027

From these results, it appears that out of the three atoms of oxygen contained in 1 mole of potassium iodate, only two are taken up for the primary oxidation of indigo carmine to isatin sulphonate, the third atom being utilised for the formation of the new substance which has the property of liberating iodine from potassium iodide.

The new oxidising substance does not appear to be iodine monochloride. When iodine monochloride is treated with potassium thiocyanate, the following reaction[10] takes place:

$$3\,KCNS + 3\,ICl \rightarrow 3\,KCl + I(CNS)_3 + I_2$$

The iodine produced in this reaction can be tested with starch. Blank experiments by the present authors have shown that it is possible to utilise this test for the qualitative detection of iodine monochloride up to a concentration limit of 1 ml of 0·005*M* solution. Since this test is not answered by the solution left at the end of the titration of indigo sulphonate with potassium iodate, the authors believe that the new oxidising species formed is iodo-isatin, with the iodine attached to the carbonyl group, and is not the nuclear iodine-substituted isatin, because it is not likely that the nuclear substituted isatin can liberate iodine from potassium iodide. It may be conjectured that this iodo-isatin may be formed through the medium of iodine monochioride, because such a hypothesis explains the catalytic action of chloride ion on the oxidation of indigo

carmine by iodate in a sulphuric acid medium, which will be discussed in the next section. In this connection it is interesting to note that when solid isatin is treated with iodine monochloride it gives 5-iodo-isatin.

During the primary process of the oxidation of indigo carmine by potassium iodate, iodic acid may decompose as follows:

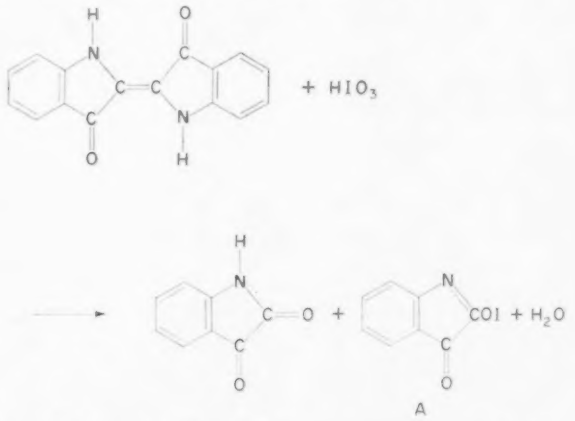
$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O.$$

The hydriodic acid (I^- ion) formed in this step may undergo further reaction with iodate in the presence of chloride ion:

$$IO_3^- + 2I^- + 3Cl^- + 6H^+ \rightarrow 3ICl + 3H_2O.$$

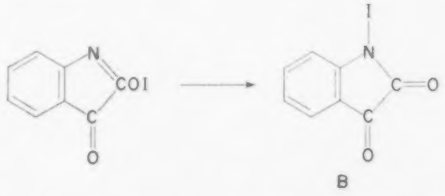
The iodine monochloride (I^+) then reacts with isatin sulphonate to give the corresponding iodo-isatin.

The overall reaction can therefore be represented by:



A

This form of the iodo-isatin, having structure A, may isomerise into *N*-iodo-isatin, having structure B, as shown below:



B

Iodo derivatives of isatin having structures A or B do not appear to have been described in the literature.

Thus, of the three atoms of oxygen in iodic acid two are utilised for the oxidation of 1 mole of indigo to give 2 moles of isatin, and the third oxygen atom is utilised for the conversion of one of the isatin molecules into *N*-iodo-isatin. The *N*-iodo-isatin (unlike the nuclear substituted isatin) is capable of liberating iodine from acidified potassium iodide. It is perhaps only by this hypothesis that we can reconcile the two sets of results: (1) the consumption of three atoms of oxygen (1 mole of potassium iodate) per mole of indigo in the direct titration, and (2) the consumption of only two

atoms of oxygen (2/3 mole of potassium iodate) per mole of indigo in the indirect method of determination with potassium iodate.

Direct Titration of Indigo Carmine with Potassium Iodate in a Sulphuric Acid–Hydrochloric Acid Medium

An extended study has been made of the influence of sodium chloride and hydrochloric acid in a sulphuric acid medium on the speed of oxidation of indigo with potassium iodate. The results obtained are given in Table IV.

TABLE IV. 3 ML OF INDIGO SULPHONATE + 6·3 ML OF 20*N* SULPHURIC ACID + X ML OF CONCENTRATED HYDROCHLORIC ACID OR 2*M* SODIUM CHLORIDE + 10 ML OF 0·021*N* POTASSIUM IODATE SOLUTION + WATER TO MAKE UP TO 50 ML.

Overall concentration of sulphuric acid, *N*	Overall concentration of hydrochloric acid, *M*	Overall concentration of sodium chloride, *M*	Time taken for the complete oxidation of indigo
2·56	nil	nil	Very slow
2·56	0·02	nil	12 min
2·56	0·04	nil	10 min
2·56	0·10	nil	14 min
2·56	0·20	nil	19 min
2·56	0·30	nil	26 min
2·56	0·50	nil	33 min
2·56	0·75	nil	40 min
2·56	1·50	nil	60 min
2·56	2·00	nil	22 min
2·56	3·00	nil	3 min
2·56	4·00	nil	5 sec
2·06	nil	nil	Very slow
2·06	nil	0·02	15 min
2·06	nil	0·04	10 min
2·06	nil	0·10	11 min
2·06	nil	0·20	18 min
2·06	nil	0·50	dye salted out
2·06	nil	1·00	dye salted out

From the results, it is seen that the reaction is quite rapid in a medium containing 2·56*N* sulphuric acid and 4·0*N* hydrochloric acid at the end. Hence, experiments have been carried out to see if a direct titration of indigo is possible with potassium iodate in such a medium. It was observed that the titration can be performed at normal speed, the disappearance of the blue of the indigo being quite sharp at the end-point. A large number of titrations carried out in this way show that the amount of potassium iodate required per mole of indigo is very nearly 1 mole. The results are given in Table.V.

In all these titrations, the residual titration mixture is suitably diluted to give an acid concentration of 1*N*, and treated with a sufficient excess of potassium iodide, the liberated iodine then being titrated with a standard solution of sodium thiosulphate, using starch as indicator. Such experiments have shown that the amount of iodine liberated corresponds to 1/3 of the amount of potassium iodate consumed in the direct titration. In view of these findings, it is considered that the mechanism of the

oxidation of indigo sulphonic acid in a mixed acid medium is similar to the one proposed for the reaction in a 6*N* hydrochloric acid medium. A comparison of the results in Tables III and V shows that titrations of indigo sulphonate in a 6*N* hydrochloric acid medium give results lying within 0·2% to 1·7% of stoichiometry as compared with a variation of 1·3% to 2·0% shown by the results of experiments in a mixed sulphuric-hydrochloric acid medium. The stoichiometric relationship observed in these iodate titrations is in sharp contrast with the titrations of indigo sulphonate with potassium permanganate or cerium^{IV} sulphate, which give values deviating rather widely from the stoichiometry.

TABLE V. X ML OF INDIGO SULPHONATE (ABOUT $7{\cdot}0 \times 10^{-3}M$) + THE REQUISITE VOLUMES OF CONCENTRATED HYDROCHLORIC ACID AND 20*N* SULPHURIC ACID TO MAKE UP TO 4*N* AND 2·5*N* RESPECTIVELY AT THE END OF THE TITRATION. THE MIXTURE IS TITRATED WITH $8{\cdot}882 \times 10^{-3}M$ OR 0·0533*N* POTASSIUM IODATE SOLUTION; TOTAL VOLUME AT THE END OF THE TITRATION IS ABOUT 50 ML.

Indigo taken, *millimoles*	Potassium iodate consumed, *millimoles*	Potassium iodate consumed per mole of indigo, *moles*
0·02231	0·02203	0·987
0·02975	0·02931	0·985
0·03718	0·03659	0·984
0·04463	0·04378	0·981
0·05206	0·05116	0·983
0·05950	0·05828	0·980
		Average = 0·983

Zusammenfassung—Bedingungen wurden gefunden, unter denen Indigosulfonsäure mit Kaliumjodat bei Zimmertemperatur direkt titriert werden kann. Die Titration wird in einer Lösung durchgeführt, die 6–8 n in Salzsäure ist. Die blaue Farbe des Indigo verschwindet im Endpunkte sehr scharf und eine gelbe Lösung hinterbleibt. Ein Mol Indigo konsumiert ziemlich nahe ein Mole Kaliumjodat. Die Redoxreaktion ist sehr langsam, wird aber durch Chloridionen erheblich beschleunigt. Die direkte Titration ist auch in einem Medium von Salz- und Schwefelsäure von geeigneter Konzentration möglich. Die Stöchiometrie dieser Titration ist in striktem Gegensatz zu der in der Indigobestimmung mit Permanganat oder Cerisulfat gefundenen. Evidenz existiert für das Auftreten einer neuen Jodverbindung des Isatinsulfonats während des Ablaufes der Redoxreaktion. Die neue Verbindung ist imstande Jodid quantitativ zu Jod zu oxydieren.

Résumé—Les auteurs ont mis au point les conditions de dosage direct de l'acide indigosulfonique par l'iodate de potassium à la température ambiante. Le titrage peut être réalisé en milieu acide chlochydrique 6–8 N. La couleur bleue de l'indigo disparaît nettement au point équivalent, donnant une solution jaune clair. Une molécule-gramme d'indigo consomme très approximativement une molécule-gramme d'iodate de potassium. La réaction du sulfonate d'indigo sur l'iodate de potassium est très lente, mais elle est accélérée notablement par l'ion chlorure. Le titrage direct du sulfonate d'indigo est aussi possible dans un milieu acide mixte contenant les acides sulfurique et chlorhydrique à des concentrations convenables. La stoechiométrie observée dans ces titrages est en contraste frappant avec les écarts mentionnés dans les titrages du sulfonate d'indigo par le permanganate de potassium et le sulfonate cérique. Les auteurs ont obtenu la preuve de la formation d'un nouveau type de dérivé du sulfonate d'isatine dans la réaction du sulfonate d'indigo et de l'iodate de potassium. Le nouveau sulfonate d'iodoisatine est capable de libérer quantitativement l'iode de l'Iodure de potassium.

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POTENTIOMETRIC DETERMINATION OF TITANIUM^{III} WITH VANADIUM^{IV}

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Summary—Conditions have now been established for the accurate potentiometric determination of titanium^{III} with vanadium^{IV} sulphate in a 1·0*N* hydrochloric acid medium and a carbon dioxide atmosphere at room temperature (28°). The potentials at a bright platinum-wire electrode have been found to attain stable values within 1 min after the addition of each portion of the vanadium^{IV} sulphate solution, if the titration mixture contains oxalic acid at an overall concentration of 0·06*M* to 0·1*M*. In the absence of oxalic acid the potentials show considerable drift with time. Tartaric, citric and malic acids also exert some beneficial effect but their action is not so pronounced as that of oxalic acid. This investigation is perhaps the first one to cover the use of vanadium^{IV} as an oxidimetric titrant.

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JONES and Colvin[1] calculated the standard potential of the V^{IV}/V^{III} couple to be +0·337 V at 25°. Syrokomskii and Avilov[2] determined the formal potential of this system in dilute sulphuric acid as +0·359 V ± 0·002 V. The potential of the Ti^{IV}/Ti^{III} couple in 1*M* hydrochloric acid is reported to have a value of −0·09 V by Lingane.[3]

In view of the sufficiently wide difference in the potentials of the vanadium^{IV}/vanadium^{III} and titanium^{IV}/titanium^{III} couples, the following reaction may be expected to take place in acidic media at room temperature:

$$V^{IV} + Ti^{III} \rightarrow V^{III} + Ti^{IV}$$

We have, therefore, attempted the potentiometric titration of titanium^{III} with vanadium^{IV} sulphate solution in a 1·0*N* hydrochloric acid medium. Titration was not possible because of the difficulty experienced in the attainment of stable potentials at the platinum indicator electrode after the addition of each portion of the titrant. However, the addition of sufficient acid was found to produce fairly stable potentials even at room temperature. Consequently, it was found possible to carry out the rapid potentiometric titration of titanium^{III} with vanadium^{IV} sulphate solution in a 1·0*N* hydrochloric acid medium, in the presence of oxalic acid. The visual titration of titanium^{III} with vanadium^{IV} using phenosafranine, safranine-T and neutral red as internal indicators was not successful. Although the reduction of the indicator by titanium^{III} was rapid in the presence of oxalic acid, the oxidation of the reduced indicator by vanadium^{IV} was very slow, with the result that the end-point was overstepped.

EXPERIMENTAL

Reagents

Titanium^{III} solution: The sample of titanium^{III} chloride solution employed in this investigation was of analytical reagent quality supplied by May & Baker, London. It was tested and found to be free from iron^{II}. A 0·05*N* solution of titanium^{III} in 2*N* hydrochloric acid solution was prepared from this sample and stored in the customary manner in an atmosphere of carbon dioxide. It was standardised by adding an aliquot volume to an excess of iron^{III} alum solution and titrating the iron^{II} formed with standard potassium dichromate solution, using diphenylbenzidine as internal indicator.

Vanadium^{IV} solution: Vanadium^{IV} sulphate was prepared by reducing the requisite quantity of ammonium vanadate (AnalaR, B.D.H.) with sulphur dioxide, removing the excess of sulphur dioxide by passing carbon dioxide, and diluting the solution to a known volume to give an approximately 0·05*N* solution. The strength of the solution was also checked by titration with standard potassium permanganate at 50–60°.

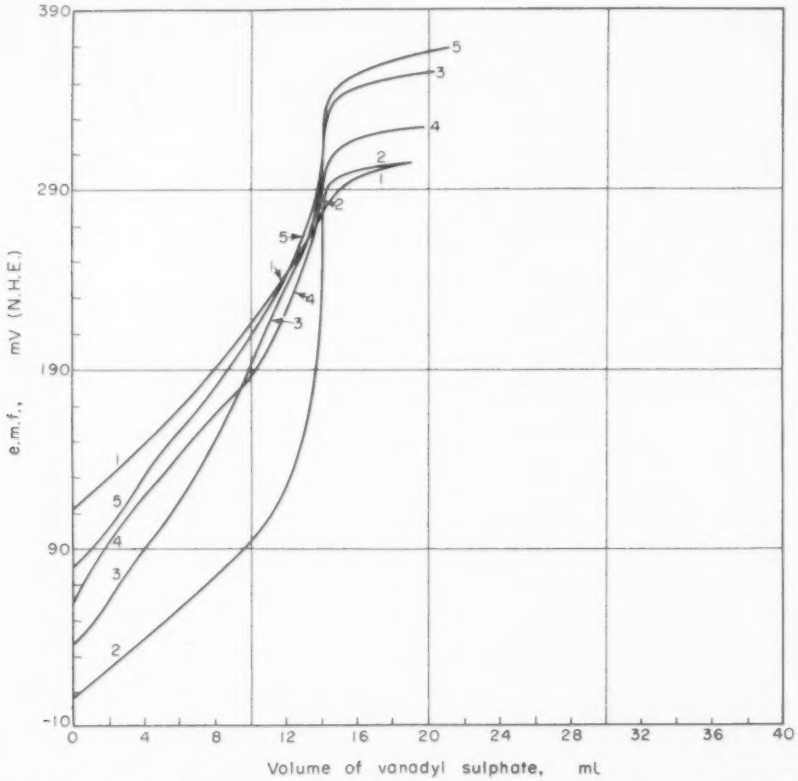

FIG. 1.—Effect of oxalic acid, citric acid, tartaric acid and malic acid on the potentiometric titration of titanium^{III} with vanadium^{IV} sulphate, in 1·0*N* HCl, at 28° (10·0 ml of Ti^{III} ≡ 14·04 ml of 0·04863*N* vanadium^{IV} sulphate).

E–V curves in the presence of:

1. Nil added.
2. 0·1*M* oxalic acid.
3. 0·1*M* citric acid.
4. 0·1*M* tartaric acid.
5. 0·1*M* malic acid.

Apparatus

The titrations were carried out in an atmosphere of carbon dioxide. A bright platinum wire dipping in the titration mixture was used as an indicator electrode, a saturated calomel electrode serving as the reference electrode. The two halves of the cell were connected through a saturated potassium chloride bridge. The potentials were measured using a Cambridge potentiometer graduated in mV in conjunction with a Cambridge galvanometer. The titration mixture was stirred with the help of a B.T.L. magnetic stirrer.

RESULTS AND DISCUSSION

The potentials were not found to attain steady values rapidly after the addition of each portion of the vanadium^{IV} solution but showed considerable drift. Curve 1 in

Fig. 1 was plotted using potentials recorded after waiting for an arbitrary period of 3 min. From the shape of the curve it is evident that the equivalence point in the titration cannot be ascertained. In this connection, it is interesting to note that Kolthoff and Tomiček[4] observed that the theoretical equivalence point was not obtained for the second stage in the potentiometric titration of vanadium^{V} with titanium^{III}; this corresponds to the reduction of vanadium^{IV} to vanadium^{III} by titanium^{III}. They found that this second stage of the titration was improved when carried out at 50–60° in the presence of Rochelle salt. Hence, we carried out titrations of titanium^{III} with vanadium^{IV} in the presence of citric, tartaric, malic and oxalic

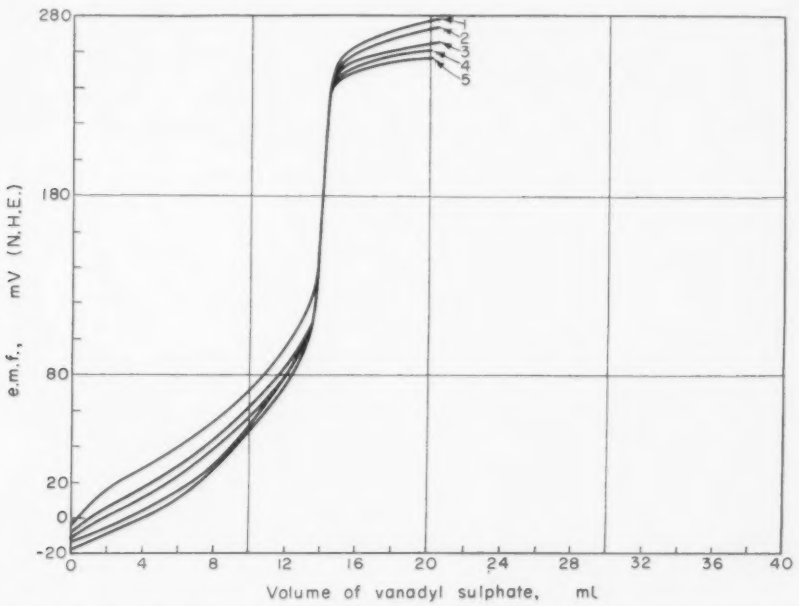

FIG. 2.—The effect of varying the concentration of oxalic acid on the potentiometric titration of titanium^{III} with vanadium^{IV} sulphate, in 1·0*N* HCl at 28° (10·0 ml of Ti^{III} = 14·04 ml of 0·04863*N* vanadium^{IV} sulphate).
E–V curves in presence of:
1. 0·15*M* oxalic acid.
2. 0·10*M* oxalic acid.
3. 0·06*M* oxalic acid.
4. 0·03*M* oxalic acid.
5. 0·01*M* oxalic acid.

acids. Curves 3, 4 and 5 in Fig. I were obtained for the titration of titanium^{III} with vanadium^{IV} in 1*N* hydrochloric acid, in the presence of 0·1*M* citric, tartaric or malic acid. Even in these titrations the potentials were found to drift with time, but they attained moderately stable values 3 min after the addition of each portion of the vanadium^{IV} solution. These curves show that the presence of these acids produces some improvement in the titration in the order, tartaric acid > citric acid > malic acid. The improvement even with tartaric acid is not, however, sufficient for a rapid titration to be conducted at room temperature. Addition of oxalic acid produced fairly constant potentials within 1 min. Curve 2 in Fig. 1 was plotted using results obtained in the presence of 0·1*M* oxalic acid, and this curve shows that a rapid and

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accurate titration of titanium^{III} with vanadium^{IV} is possible at room temperature. The rise in potential at the equivalent point has been observed to be about 120 mV for 0·05 ml of the vanadium^{IV} solution.

Effect of varying the concentration of oxalic acid

The influence of varying concentrations of oxalic acid on the course of the potentiometric titration is shown by the curves in Fig. 2. Good titrations are possible at all concentrations of oxalic acid varying from 0·01*M* to 0·15*M*, the overall concentration of titanium^{III} in the experiments being 0·014 mole per litre. Blank experiments showed that oxalic acid does not interfere with the accuracy of the titration.

Recommended procedure

Fifty ml of 1*N* hydrochloric acid, containing oxalic acid at an overall concentration of 0·06 to 0·1*M* are transferred to a reaction vessel fitted with a stopper having 6 holes, to accommodate the inlet and outlet tubes for passing carbon dioxide, the saturated potassium chloride bridge (containing the saturated calomel half cell), the platinum indicator electrode and the two burettes (one burette containing vanadium^{IV} sulphate solution and the other burette connected to the titanium^{III} chloride reservoir). The titration mixture may be stirred with a B.T.L. magnetic stirrer. Carbon dioxide is passed through the vessel for 10 min to free it from air. An aliquot of the titanium^{III} chloride solution is added, and the mixture is then titrated with the vanadium^{IV} sulphate solution, while continuing the passage of carbon dioxide through the vessel. The potentials of the system are measured at suitable intervals (1 min after the addition of each portion of vanadium^{IV} sulphate solution). A curve is plotted showing the relation of the potential to the volume of the vanadium^{IV} solution, and the equivalence point is noted from the curve.

Typical results are presented in Table I.

TABLE I. POTENTIOMETRIC DETERMINATION OF TITANIUM^{III} WITH VANADIUM^{IV} SULPHATE

Amount of titanium^{III}, *millimoles*	
Taken	Found
0·1036	0·1034
0·2072	0·2074
0·2590	0·2592
0·3648	0·3660
0·5180	0·5178
0·6236	0·6232

From the results in Table I, it will be seen that the recommended procedure is capable of giving results accurate to ±0·2%.

Zusammenfassung—Bedingungen wurden ausgearbeitet zur volumetrischen Bestimmung von Titan (III) mit Vanadin(IV) sulfat in 1.0 n Salzsäure, bei Zimmertemperatur unter Kohlendioxydschutz und mit potentiometrischem Endpunkt. Es wurde gefunden, dass das Potential an einer blanken Platinelektrode nach etwa einer Minute nach Zugabe des Titrationsmittels stabil ist, wenn die Lösung etwa 0–6 bis 1.0 molar in Oxalsäure ist. In Abwesenheit von Oxalsäure zeigt die Potentialeinstellung erhebliche Zeitabhängigkeit. Auch Wein- und Citronensäure haben eine stabilisierende Wirkung, sie ist jedoch bei weitem nicht so ausgeprägt, wie die der Oxalsäure. Die beschriebene Methode ist eine der ersten, bei der Vanadin(III) als oxidimetrisches Titrationsmittel verwendet wird.

Résumé—Les auteurs ont mis au point les conditions du dosage du titane(III) par le sulfate de vanadium(IV) en milieu acide chlorhydrique N sous atmosphère d'anhydrique carbonique à la température ambiante, le point équivalent étant déterminé par potentiométrie. Ils ont trouvé que les potentiels à une électrode de platine poli atteignaient des valeurs stables moins d'une minute après l'addition de chaque portion de la solution de sulfate de vanadium(IV) si la solution à titrer contient de l'acide oxalique à une concentration globale de 0,6–1*M*. En l'absence d'acide oxalique les potentiels varient considérablement avec le temps. Les acides tartrique, citrique et malique exercent aussi un effet favorable, mais leur action n'est pas aussi prononcée que celle de l'acide oxalique. Cette méthode est un des premiers exemples de l'utilisation du vanadium(IV) comme agent titrant en oxydimétrie.

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Talanta, 1961, Vol. 8, pp. 552 to 557. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Spectrophotometric study of the complex of lanthanum and alizarin Red S

(*Received* 19 *December* 1960. *Accepted* 7 *January* 1961)

THE complexes of alizarin Red S and metals have been investigated by many workers: Rinehart[1] reported the spectrophotometric determination of some rare earths and yttrium with this compound. Rao and his co-workers have reported spectrophotometric studies on the complexes of the organic reagent with thorium, uranyl, yttrium, and lanthanum.[2–4] They concluded that the alizarin Red S combined with lanthanum in a mole ratio of 1:1 in 60% acetone solution.

The empirical formulae of coloured complexes in aqueous solution have generally been established by the molar ratio method,[5] the method of continuous variation,[6] or the slope ratio method.[7]

The present work suggests that the complex of lanthanum and alizarin Red S is La [Aliz.]$_2$; for the investigation a modification of the slope ratio method, based on the determination of the molar absorbance of the organic reagent α_r and of the coloured complex α_c, together with the slope ratio, was employed.

Modification of slope ratio method

If a metal ion, M, reacts with an organic reagent, R, to form a coloured complex, then

$$M + nR \longrightarrow MR_n \tag{1}$$

If the concentration of R, [R], is kept constant and that of M, [M], is varied, and if A is the absorbance with respect to a light beam of a given wavelength, [M] is the initial molar concentration of a metal ion, α is the molar absorbance, and suffixes c and r relate to the coloured complex and the organic reagent,

$$A = A_c + A_r.$$

From Beer's law

$$A = (A_r^0 - \alpha_r n[M]) + \alpha_c[M]$$

$$= A_r^0 + (\alpha_c - \alpha_r n)[M]. \tag{2}$$

Similarly, when the initial concentration of the metal ion is kept constant, and that of the organic reagent is varied, we have

$$A = \alpha_c[M] = \alpha_c \frac{[R]}{n}. \tag{3}$$

Dividing the slope of equation (2) by that of equation (3), we have

$$\frac{\text{Slope of (2)}}{\text{Slope of (3)}} = \frac{(\alpha_c - \alpha_r n)}{\alpha_c/n} = \mu. \tag{4}$$

As an approximate value for α_c, a value for α_r, and the slope ratio, μ, may be obtained experimentally. The value of n may therefore be determined.

Results and Discussion

Absorption spectra for the solution of lanthanum and alizarin Red S, when the initial concentration of alizarin Red S was held constant and that of lanthanum was varied, are given in Fig. 1. It

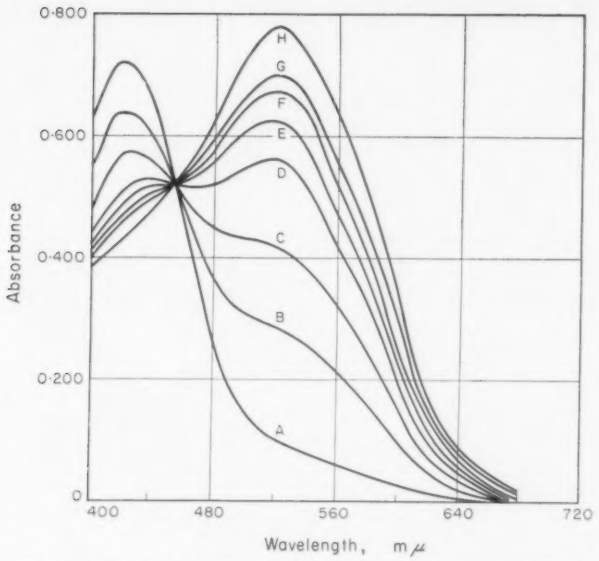

FIG. 1.—Absorption spectra for a solution of lanthanum and alizarin Red S.
Constant component (Aliz.): $2.00 \times 10^{-4}M$.
Variable component (La); A $0.00 \times 10^{-4}M$.
B $0.429 \times 10^{-4}M$, C $0.715 \times 10^{-4}M$,
D $1.00 \times 10^{-4}M$, E $1.14 \times 10^{-4}M$,
F $1.28 \times 10^{-4}M$, G $1.43 \times 10^{-4}M$,
H $1.73 \times 10^{-4}M$.

is clear that alizarin Red S forms a coloured complex with lanthanum in acetate medium of pH 4.6, since an isobestic point is shown.

If the initial concentration of lanthanum is kept constant, and that of alizarin Red S is varied, the absorption spectrum changes as shown in Fig. 2.

The absorbance of alizarin Red S in acetate medium of pH 4.6 in the visual region obeys Beer's law (Fig. 3), so that the molar absorbance of the reagent, α_r, at, for example, 520 mμ, may be calculated. For this wavelength it is found to be 430.

The curves given in Fig. 4 were obtained by plotting absorbance at 520 mμ versus molar concentration of the variable in accordance with the data shown in Fig. 1 and Fig. 2. The calculated slope ratio, μ, was 1.68. But as the molar absorbance of the coloured complex in acetate medium, determined against a reagent blank, is 7900, the value of n is 2.01.

Thus, it would appear that the alizarin Red S forms a coloured complex with lanthanum in the mole ratio of 2:1 in acetate medium of pH 4.6.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were made with a HITACHI spectrophotometer Model EPU-2 using a 1-cm transmission cell. TOADENPA Model HM-5 was used for the pH measurements.

Reagents

Alizarin Red S solution: Prepared by dissolving a known amount of the organic reagent (reagent-grade purity) in acetic acid-ammonium acetate buffer solution.

Lanthanum solution: A known weight of lanthanum oxide (99.9%, Johnson Matthey Co., Ltd., Hatton Garden, London) was dissolved in hydrochloric acid.

Buffer solution: Acetic acid-ammonium acetate mixtures were used for controlling the pH of the solution.

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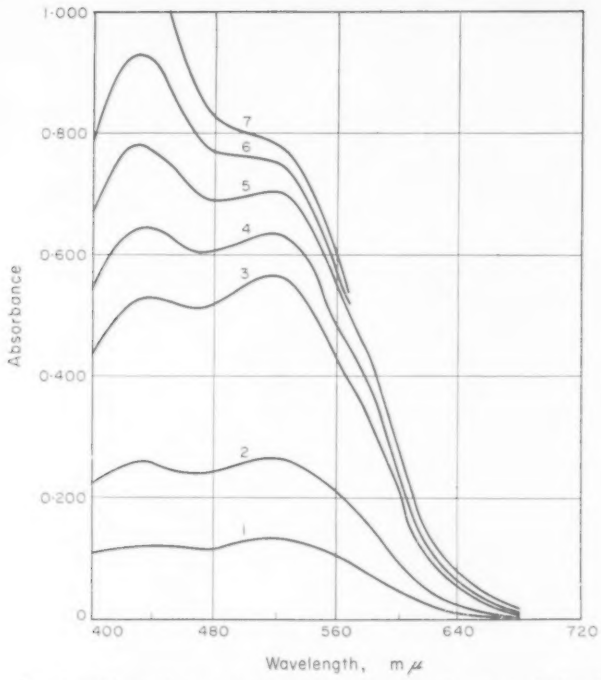

FIG. 2.—Absorption spectra for a solution of lanthanum and alizarin Red-S.
Constant component (La): $1.00 \times 10^{-4}M$ La.
Variable component (Aliz.):

1; $0.50 \times 10^{-4}M$, 2; $1.00 \times 10^{-4}M$, 3; $2.00 \times 10^{-4}M$,
4; $3.00 \times 10^{-4}M$, 5; $4.00 \times 10^{-4}M$, 6; $5.00 \times 10^{-4}M$,
7; $6.00 \times 10^{-4}M$.

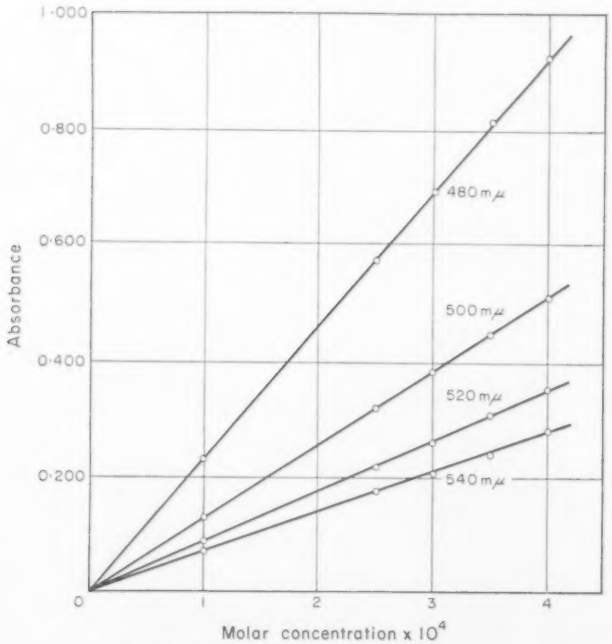

FIG. 3.—Working curve for alizarin Red S in acetate medium (pH 4.6)

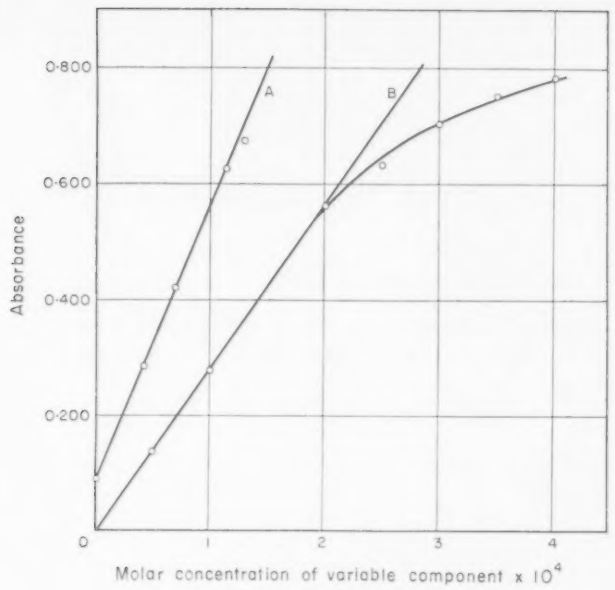

FIG. 4.—Slope ratio, at 520 mμ.
A: La varying, [Aliz.] $2 \times 10^{-4}M$,
B: Alizarin Red S varying, [La] $1 \times 10^{-4}M$.

Procedure

Colour development was carried out at room temperature in the buffer solution following Rinehart's method.[1]

For the study of the coloured complex, a given amount of lanthanum and alizarin Red S were added to the acetate buffer solution and the pH of the solution was adjusted to 4.60 with hydrochloric acid or sodium hydroxide and then diluted to 50 ml. This was followed by absorbance measurements.

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Summary—The complex of lanthanum with alizarin Red S in acetate medium has been studied spectrophotometrically since it appears to be promising for the determination of the chemical yield in radioactivation analysis of rare earth elements. At pH 4.6 (acetate buffer) the molecular ratio lanthanum: alizarin Red S is 1:2.

Zusammenfassung—Eine spetralphotometrische Studie des Lanthankomplexes von Alizarin Rot S ergab dass bei pH 4,6 (Acetatpuffer) das Verhältnis La:Farbstoff gleich 1:2 ist.

Résumé—D'après une étude spectrophotométrique du complexe formé entre le lanthane et le rouge alizarine S, les auteurs concluent que, en milieu acétate de pH 4,6, ce complexe existe dans le raport molaire La/rouge alizarine S = 1/2.

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Sur un principe de colorimétrie en milieu non aqueux—II

Emploi du bromure de *p*-nitrophénacyle pour l'identification et le dosage des acides carboxyliques

(*Received* 6 *February* 1961. *Accepted* 20 *February* 1961)

L'IDENTIFICATION des acides carboxyliques, sous forme d'esters, est le plus souvent effectuée à l'aide des acétophénones α-halogénées.[1]

Selon nos essais,* la mise en œuvre du dérivé *p*-nitré correspondant, c'est-à-dire du bromure de *p*-nitrophénacyle qui n'avait pas encore été retenue, conduit aisément à des esters dont les points de fusion sont souvent supérieurs à ceux des esters de phénacyle déjà décrits (esters formique: 142°,5; acétique: 123°; propionique: 108°, 5; butyrique: 45°, 5; benzoïque: 147°, 5; phénylacétique: 84°; oxalique: 226°; succinique: 184°).

La présence d'un groupe nitré permet par ailleurs une identification colorimétrique en milieu non aqueux. Sur un principe précédemment énoncé,[2] il est en effet possible, à partir de l'acide carboxylique, de procéder à la formation de l'ester puis, par l'emploi d'un solvant, de développer d'emblée une coloration, sans extraction préalable ni élimination de l'excès de réactif. Après acylation par le bromure de *p*-nitrophénacyle en présence d'acétonitrile puis dilution dans le diméthylsulfoxyde, la diéthylamine développe une coloration violette (550 mμ) qui n'est pas observée en absence de carboxyle. La méthode étant quantitative, des dosages peuvent être effectués à partir de prises d'essai de l'ordre du centième de milligramme (tableau I).

TABLEAU I

Acides dosés	Prise d'essai pour obtenir une densité optique de 0,3 à 550 mμ en cuve de 1 cm. μg
acétique	7
benzoïque	14
butyrique	12
citrique†	90
formique	10
phénylacétique	19
propionique	11
oxalique†	26
succinique†	40

Mode opératoire

L'acide, en solution aqueuse, est neutralisé par du carbonate de sodium. A la prise d'essai, dans 0,25 cm³ de solution, on ajoute 0,1 cm³ de solution à 0,3 pour cent de bromure de *p*-nitroacétophénone[3]

* effectués avec la collaboration de Mlle G. CLEMENT.
† Pour les diacides, la concentration du réactif doit être portée à 0·5 pour cent en bromure de *p*-nitrophénacyle.

dans l'acétonitrile*. Après repos de dix minutes à température ordinaire, on ajoute 5 cm³ de diméthylsulfoxyde puis, après cinq minutes de contact, 0,5 cm³ de diéthylamine. Lecture immédiate à 550 mμ.

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Résumé—En complément des tests d'identification en milieu non aqueux des groupes hydroxyle, carbonyle et amine primaire, précédemment décrits (*ibid.*, 1960, **5,** 216), il est possible de caractériser les acides carboxyliques sous forme d'esters de *p*-nitrophénacyle. Ces esters développent en effet, sans extraction ni élimination de l'excès de réactif, une coloration avec la diméthylamine lorsqu'on opère dans un mélange d'acétonitrile et de diméthylsulfoxyde. Des dosages peuvent être effectués sur des prises d'essai de l'ordre du centième de milligramme.

Summary—Supplementing the identification tests in non-aqueous medium for hydroxyl, carbonyl and primary amine groups, already described (*Talanta* 1960, **5,** 216) it is possible to characterise carboxylic acids in the form of the *p*-nitrophenacyl esters. These esters, without the necessity for extraction or of the elimination of excess reagent, develop a colour with dimethylamine when treated in mixture with acetonitrile and dimethylsulphoxide. Tests can be carried out on amounts of the order of 0·01 mg.

Zusammenfassung—Teste zur Identifizierung von Hydroxyl- Carbonyl- und primären Aminogruppen in nichtwässrigem Medium wurden bereits beschrieben (*Talanta* 1960, **5,** 216). Ergänzend hierzu wird die Möglichkeit gezeigt Carboxylsäuren in der Form ihrer *p*-Nitrophenacylester zu charakterisieren. Diese Ester entwickeln eine Farbe mit Dimethylamin, wenn die Mischung mit Acetonitril und Dimethylsulfoxyd behandelt wird. Eine Extraktion oder Entfernung des Überschusses an Reagens ist nicht nötig. Die Probe kann mit Mengen in der Grössenordnung von einem Hundertstel eines Milligramms durchgeführt werden.

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* L'acétonitrile doit être neutre, les traces d'acide pouvant être éliminées par distillation.

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BOOK REVIEWS

Aplicaciones analiticas del AEDT y similares. F. BERMEJO und A. PRIETO. Santiago de Compostela 1960. Pp. xii + 625. $10.00.

DIE Literatur über ÄDTE und analoge Verbindungen ist in unglaublichem Masse angewachsen und weiter in stetigem Steigen begriffen. Es ist daher äusserst begrüssenswert, dass sich die beiden Autoren der unendlichen Mühe unterzogen haben, die Flut von Mitteilungen zu sichten, zu klassifizieren und den wesentlichen Stand unseres derzeitigen Wissens über die analytischen Anwendungen dieser Substanzen in Buchform herauszugeben. Das Literaturverzeichnis umfasst 1278 (!) Zitate wissenschaftlicher Mitteilungen und darüber hinaus noch etliche Monographien.

Das Buch ist als äusserst gelungen zu bezeichnen und wird sowohl dem praktisch Arbeitenden als auch dem theoretisch Interssierten grösste Hilfe bedeuten. Besonders die Arbeitsvorschriften, die etwa die Hälfte des Werkes beanspruchen, zeigen deutlich, dass die Autoren auf dem Gebiete aktive tätig sind und sowohl bei Auswahl als auch Beschreibung der Methoden autoritativ kritisch gesichtet haben.

Auch der theoretische Teil ist als gelungen zu bezeichnen; er ist klar gegliedert und logisch aufgebaut. Jedoch wird sich ein mit der Materie weniger Vertrauter manchmal recht schwer zurechtfinden. Die Verfasser haben es leider unterlassen Nomenklatur, Symbole und Beschriftung der Abbildungen zu vereinheitlichen und die entsprechenden Zeichen einfach gemäss der jeweiligen Originalarbeit übernommen. Dies führt dazu, dass wechselweise Stabilitäts- oder Dissoziationskonstanten der Komplexe verwendet werden. Einer der Faktoren zur Berechnung der scheinbaren Stabilitätskonstanten wird bald als α, α_H oder Φ geführt. In den Abbildungen auf Seite 68 und 69 werden die Ordinaten der Diagramme für die Absorptionskurven wahllos als Absorption, Optische Dichte, Absorptionskoeffizient oder % Transmission bezeichnet; letzteres zusätzlich bald von unten nach oben bald umgekehrt aufgetragen. Manche der Diagramme (besonders 78, 79) sind zu klein geraten und können selbst mit einer Lupe kaum entziffert werden. Eininge Druckfehler wirken störend. Die Verbindung XII (Seite 3) ist keine Penta- sondern eine Tetraessigsäure. Der Titel des Buches selbst enthält einmal die Phrase "AEDT y analogos" (Front des Schutzumschlages) ein andermal jedoch "AEDT y similares" (Rücken). Derlei Dinge sind aber wohl bei der Abfassung solch eines Werkes unvermeidlich und sollten sich bei einer sicherlich sehr bald fälligen Neuauflage ausmerzen lassen.

Diese und einige andere Mängel minderer Art tun der Gesamtanlage des Buches jedoch keinerlei Abbruch. Das Werk kann nicht nur wärmstens empfohlen werden sondern wird in Kürze sicherlich ein "Muss" in der Bibliothek jede Analytikers sein.

H. FLASCHKA

Advances in Polarography (Proceedings of the Second International Congress held at Cambridge, 1959). Three volumes. Edited by IAN S. LONGMUIR. Pp. 1204. Pergamon Press (Oxford, London, New York, Paris) 1960. £15 per set.

THIS is a collection in three volumes of about 100 papers presented at an international Congress of Polarography held in Cambridge in August 1959. The collection of papers by authors of many nationalities is probably representative of current thought in the many different fields of polarography.

As pointed out by the editor, the assignment of the papers to particular volumes is difficult because of the diversity of the subject matter. However, the first volume appears to be concerned mainly with

papers which deal with developments in new polarographic apparatus, fundamental theory and instrumental techniques. The second volume deals mainly with industrial applications, including some fundamental studies, and the third volume comprises more fundamental studies and applications.

The Congress was held to honour the 70th birthday of Professor Heyrovsky and he is the contributor of the first paper entitled *Oscillographic Polarography*. During the past few years the Polarographic Institute in Prague has made a special study of oscillographic polarography and most of the results of their work on this subject have been published in German; this *résumé* in English is therefore particularly welcome. The various aspects of polarography which are studied in Prague are well represented in these volumes and there are many Czech contributors. Apart from papers on instruments and techniques, papers appear on what seem to be unrelated topics, such as the study of polarographic kinetic currents in Volume 2 and the application to the purely organic problem of the polarographic reduction of the single carbon-nitrogen bond in Volume 3.

A valuable feature of the contributions to these volumes is their up-to-date nature. Thus papers on current trends in apparatus are prominent and a.c. instruments such as the cathode ray polarograph are dealt with by a number of authors.

Subjects which have formed the basis of lectures which will be of general interest to the practical worker in the various fields of chemistry include *The Stability of Metal Complexes and their Measurement Polarographically* by H. M. N. H. Irving; *The Hanging Drop Method* by W. Kemula; *Biological and Medical Applications* by I. S. Longmuir; *A Polarograph for Oxygen Estimation in Respiring Biological Systems* by N. L. Gregory; *Polarographic Behaviour of Nitrate and Nitrite in Strongly Acidic Mediums* by J. Masek; *The Application of the Cathode-ray Polarograph to the Analysis of Semi-conductors* by Franz-Arthur Pohl.

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Polarography in organic solvents has received attention, thus there is a novel paper on studies of dimethylformamide extracts of coal as an aid to the study of its structure. There is also a paper on *Polarography in Molten Nitrates*.

There are two interesting papers contributed by German workers on the application of polarography to studies of the eye.

To the person who is interested only in the theoretical side of polarography there is much material for examination and assessment.

There is no subject index to the books; although this might have been difficult to compile in this type of work I should have thought that it would have been worthwhile. There is an author index which includes not only those who read papers and took part in discussions but also authors of papers appearing as references. This seems to be an unnecessary trouble to go to and it might have been better to have kept solely to authors who took part in the proceedings of the Congress.

I recommend that all who use polarography or have an interest in the subject should possess these three volumes. I congratulate the Editor and also the Publisher for the excellent printing standards, although the time taken to publish does seem to have been unnecessarily long.

A. F. Williams

Talanta, 1961, Vol. 8, pp. 560 to 562. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Wednesday–Saturday 2–5 *August* 1961: *Twenty-first Conference of the International Union of Pure and Applied Chemistry*. Montreal.

Sunday–Saturday 6–12 *August* 1961: *Eighteenth International Congress of Pure and Applied Chemistry*. Montreal.

GERMANY

Wednesday–Saturday 13–16 *June* 1962: **Analytical Chemical Division, Gesellschaft Deutscher Chemiker** and **Gas Chromatography Discussion Group, Hydrocarbon Research Group of Institute of Petroleum:** *Fourth International Symposium on Gas Chromatography* and *Forty-first meeting of European Federation of Chemical Engineering*. Hamburg, Germany.

The main language of the meeting will be English and the papers presented should be in a form similar to those at the former Symposia on Gas Chromatography. They will be classified under three headings:

1. Theory
2. Apparatus and Techniques
3. Applications.

Preliminary registration for attending the symposium should be sent as soon as possible to Gesellschaft Deutscher Chemiker, c/o Dr. W. FRITSCHE, Frankfurt/M, Postfach 9075, Germany.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Montag 30 *Oktober-Freitag* 4 *November* 1961: **Institut für physikalische Stofftrennung der Deutschen Akademie der Wissenschaften zu Berlin,** Leipzig (DDR), Permoser Straße: Internationale Arbeitstagung, Thema *Trennung, Anwendung und Analyse stabiler Isotope sowie physikalische und chemische Eigenschaften isotoper Systeme*.

Montag-Mittwoch 27–29 *November* 1961: **Deutsche Akademie der Wissenschaften, Sektion für Physik, Unterkommission Leuchtstoffe:** Arbeitstagung, Thema *Physik und Chemie der Kristallphosphore*. Berlin.

Vortragsanmeldungen werden erbeten an die Deutsche Akademie der Wissenschaften zu Berlin, Sektion fur Physik, Unterkommission Leuchtstoffe, Berlin W 8, Otto-Nuschke-Straße 22/23.

HUNGARY

After the Congress on Analytical Chemistry held in Buda-Pest on 24–29 April, 1961, Professor R. Belcher, Professor L. Gordon and Professor I. P. Alimarin were invited to Prague as guests of the Czechoslovak Chemical Society. Together with Dr. R. A. Chalmers of the University of Aberdeen they read short papers on various aspects of analytical chemistry at a morning seminar of the Czechoslovak Chemical Society in the Lecture Theatre of the Czechoslovak Academy of Sciences.

In the evening, a small dinner-party was held in honour of the visitors. The guests were Professor R. Belcher, President of the Analytical Chemistry Section of IUPAC, Professor L. Gordon, Secretary

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of the Analytical Chemistry Section of IUPAC, Professor I. P. Alimarin, member of the Analytical Section Committee and Dr. R. A. Chalmers, University of Aberdeen. Their hosts were Dr. G. Körbl, Professor F. Cuta, Dr. and Mrs. R. Přibil, Dr. and Mrs. J. Zyka.

After the Dinner, the following toast to the guests was made by Professor Cuta and it was thought to be of sufficient interest to be reproduced here:

Our dear guests,

I take the liberty to express my hearty thanks to you from the Czechoslovak Academy of Sciences and from the Czechoslovak Chemical Society for your delivered lectures in which you brought us in the fields you were interested in. Instead of going directly back to your home-countries from Hungary, you decided to spend with us your precious time not speaking about the toil accompanying it.

We appreciate very much your staying with us because we are not having much opportunity to come in deeper contact with authorities and famous workers in different branches of Science.

There exists a language barrier acting like a membrane among different phases preventing their particles to get into a closer contact in order to share their properties. We do not want, however, to stay as a separated phase, as it is done in analytical procedure, when performing separation prior to determination. We wish to be active in this process, we wish to be estimated rather by the activity than by the separation.

We would like, the forces working in the analytical process for separation of the components of a substance to be analysed, to act just in the opposite way, than we are using them in analytical chemistry. That is to act for the unification of the phases to help them distributing their energies, to enable their particles, to cooperate each with the other.

This is the reason why I take the liberty to drink the toast to our cooperation not only in the science of analytical chemistry, but also in the mutual understanding and friendly relations between us and between our own countries. I drink the toast also to your health.

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UNITED KINGDOM

Monday–Thursday 9–12 April 1962: **Feigl Anniversary Symposium.** Birmingham, England.

An International Symposium on Analytical Chemistry, sponsored by the Midlands Section of the Society for Analytical Chemistry, will be held in honour of Professor Fritz Feigl to commemorate his 70th birthday. Further details will be announced later.

Symposium Secretary: Mr. M. L. RICHARDSON, c/o John and E. Sturge Ltd., Lifford Chemical Works, Kings Norton, Birmingham, 30, England.

B.S.I. News announces the following new British Standards:

B.S. 3338: Methods for the sampling and analysis of tin alloys:

Part 3: 1961: Determination of antimony in ingot tin (photometric method). This specifies reagents required, recommended methods of sampling and test procedures for the determination of antimony in ingot tin having an antimony content up to 0.25%. (Price 3s.)

Part 4: 1961: Determination of copper in ingot tin and tin-lead solders (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of copper in ingot tin and tin-lead solders having a copper content from 0.01 to 0.4%. (Price 3s.)

Part 5: 1961: Determination of lead in ingot tin and tin-antimony solders (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of lead in ingot tin and tin-antimony solders having a lead content up to 0.9%. (Price 3s.)

Part 6: 1961: Determination of copper in high purity ingot tin (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of copper in high purity ingot having a copper content up to 0.04%. (Price 3s.)

Part 8: 1961: Determination of bismuth in ingot tin, tin-lead solders and white metal bearing alloys (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of bismuth in ingot tin, tin-lead solders and white metal bearing alloys having a bismuth content up to 0.12%. (Price 3s.)

B.S. 1014: 1961: Pigments for cement, magnesium oxychloride and concrete. This deals with chromium oxide pigments, red-iron oxide pigments, carbon black pigments, mineral black pigments, black-iron oxide pigments, yellow-iron oxide and iron hydroxide pigments (including natural ochres), brown iron-manganese oxide pigments (including sienna and umber), titanium oxide pigments (including rutile and anatase) and zinc sulphide pigments (including lithopones).

The composition and requirements of each pigment are laid down and methods of test, which include analytical procedures for the main constituents, are given in the appendices. (Price 7s.6d.)

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 16: 1961: Reporting of results. This deals with the conversion to various other bases of results obtained on the analysis sample by the methods already specified and explains how such results may be interpreted. The derivation of the calculations previously employed is given in an appendix. (Price 8s.6d.)

B.S.I. News also announces the following revised British Standard:

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 13: 1961: Tests special to coke. This deals with tests on coke which have at present no direct counterpart for coal and covers shatter index, abrasion index, bulk density, true and apparent specific gravity, reactivity (by critical air blast or as the thermal value of volatile matter) and the permitted tolerances for these determinations. (Price 7s. 6d.)

The following Amendment Slips are announced:

B.S. 1672: Methods of testing rubber latex: Part 2: 1954: Chemical and physical tests. Amendment No. 3: PD 4107. (Price 2s.)

B.S. 3156: 1959: Methods for the sampling and analysis of fuel gases. Amendment No. 1: PD 4136. (Gratis)

UNITED STATES

Monday 31 *July–Friday* 4 *August* 1961: **American Crystallographic Association:** *Summer Meeting.* University of Colorado, Boulder, Colo.

Monday–Wednesday 7–9 *August* 1961: **Denver Research Institute:** *Tenth Annual Conference on Application of X-Ray Analysis.* Park Lane Hotel, Denver, Colo.

Thursday–Friday 10–11 *August* 1961: **Society for Applied Spectroscopy, Rocky Mountain Section:** *Fourth Annual Rocky Mountain Spectroscopy Conference.* Park Lane Hotel, Denver.

Monday–Friday 14–18 *August* 1961: *Gordon Research Conference on Analytical Chemistry.* New Hampton School, New Hampton, N.H.

Monday–Friday 14–18 *August* 1961: *Gordon Research Conference on Instrumentation.* Colby Junior College, New London, N.H.

Wednesday–Saturday 23–26 *August* 1961: *Nineteenth Annual Meeting of the Electron Microscopy Society of America.* Hilton Hotel, Pittsburgh, Pa.

Sunday–Friday 3–8 *September:* **American Chemical Society:** *140th National Meeting.* Chicago, Ill.

This will include symposia on emission spectroscopy, electroanalytical chemistry and chelation in analytical chemistry. A joint symposium will be held with the Division of Cellulose Chemistry on instrumental methods for the analysis of cellulose and cellulose derivatives. Another with the Division of Agricultural and Food Chemistry will consist of a workshop on methods for pesticide residues and food additives.

Sunday–Wednesday 17–20 *September* 1961: **Extension Service Pharmacy** and **The School of Pharmacy, University of Wisconsin:** *First Annual Conference on Pharmaceutical Analysis.* King's Gateway, Land O'Lakes, Wis.

The programme will include one-day symposia on fluorometric analysis and gas chromatographic analysis, both theoretical and applied aspects of these subjects being covered. There will also be a half-day session on administrative aspects of pharmaceutical analysis and control.

Details are available from R. S. STROMEN, Pharmacy Building, University of Wisconsin, Madison, Wis.

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Talanta, 1961, Vol. 8, pp. 563. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Trifluoromethyl sulphonic acid as a titrant in glacial acetic acid systems: E. S. LANE. (1 *May* 1961).

Chelatometric determination of caesium: ARTHUR DE SOUSA. (3 *May* 1961).

Determination of hydrogen, carbon, and oxygen in zirconium powder: GEORGE NORWITZ, JOHN J. JACKIEWICZ and JOSEPH COHEN. (4 *May* 1961).

A self-sampling indicator tube for carbon dioxide: P. R. KIFF and B. F. R. PARTRIDGE. (8 *May* 1961).

Evaluation and correlation of partition parameters involved in paper chromatography: JOHN A. THOMA. (8 *May* 1961).

The gravimetric determination of scandium using mandelic acid: I. P. ALIMARIN and SHEN HAN-SI. (9 *May* 1961).

The determination of zirconium with *N*-benzoylphenylhydroxylamine: I. P. ALIMARIN and TZE YUNG-SCHAING. (9 *May* 1961).

The spectrophotometric determination of trace amounts of silver: R. M. DAGNALL and T. S. WEST. (11 *May* 1961).

Use of nickel phthalocyanine sulphonic acid as a redox indicator in cerimetry—II: Titrimetric determination of uranium^{IV} and molybdenum^{V}. G. GOPALA RAO and N. VENKATESWARA RAO. (12 *May* 1961).

Use of nickel phthalocyanine sulphonic acid as a redox indicator in cerimetry—III: Titration of ferrocyanide, hydroquinone and arsenic^{III}. G. GOPALA RAO and N. VENKATESWARA RAO. (12 *May* 1961).

Photocolorimetrische Zirkoniumbestimmung in Magnesium-Speziallegierungen mittels Morin: HANUŠ TŮMA and VLADIMÍR KABICKÝ. (12 *May* 1961).

The determination of traces of gold in samples of platinum by neutron-activation analysis: D. F. C. MORRIS and R. A. KILLICK. (16 *May* 1961).

The solubility of bis-8-quinolinolo-zinc: JAMES FRESCO and HENRY FREISER. (18 *May* 1961).

Simultaneous infrared determination of sulphate, nitrate and nitrite in water samples: IRVIN CITRON, HAN TAI, R. A. DAY, JR. and A. L. UNDERWOOD. (18 *May* 1961).

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Talanta, 1961, Vol. 8, p. 564. Pergamon Press Ltd. Printed in Northern Ireland

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NMR and EPR Spectroscopy: The staff of Varian Associates; Pergamon Press, Ltd., Oxford, 1960. Pp. viii + 288. 80s.

Advances in Polarography: Edited by I. S. LONGMUIR. Pergamon Press, Ltd., Oxford, 1960. Vol. I, pp. xiv + 407: Vol. II, pp. ix + 408–803: Vol. III, pp. 804–1204. £15.

Instability Constants of Complex Compounds: K. B. YATSIMIRSKI and V. P. VASIL'EV. Pergamon Press, Ltd., Oxford, 1960. Pp. viii + 218. 42s.

Gas Chromatography: Second International Symposium. Edited by HENRY J. NOEBELS, R. F. WALL and NATHANIEL BRENNER. Academic Press, Inc., N.Y. Academic Press, Ltd., London, 1961. Pp. xvi + 463. 114s. 6d.

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung, Part 2: Herausgegeben von der Fachgruppe Wasserchemie in der Gesellschaft Deutscher Chemiker, 3rd Edition. Verlag Chemie GMBH, Weinheim, 1960. Parts 1 and 2, DM 27.50.

Physical Chemistry: E. A. MOELWYN-HUGHES. Second edition. Pergamon Press, Ltd., Oxford, 1961. Pp. vii + 1333. 84s.

Gas Sampling and Chemical Analysis in Combustion Processes: G. TINÉ. Pergamon Press, Ltd., Oxford, 1961. Pp. xv + 94. 42s.

Computing Methods and the Phase Problem in X-Ray Crystal Analysis: Edited by RAY PEPINSKY, J. M. ROBERTSON and J. C. SPEAKMAN. Pergamon Press, Ltd., Oxford, 1961. Pp. viii + 326. 63s.

Reagent Chemicals: American Chemical Society Specifications, 1960: Edited and produced by Applied Publications, American Chemical Society, Washington, D.C., 1961. Pp. xv + 564.

X-Ray Analysis of Organic Structures: S. C. NYBURG. Academic Press, New York and London, 1961. Pp. xii + 434. $13.00. 93s.

Radioactive Contamination of Materials Used in Scientific Research: JAMES R. DEVOE. National Academy of Sciences, National Research Council, Publication 895, 1961. Pp. vii + 142.

Acta Chimica Academiae Scientiarum Hungaricae: Edited by Z. CSÚROS. Hungarian Academy of Sciences, Budapest, 1961. Vol. 26, pp. 518, 130, -Ft. Vol. 27, pp. 480, 120, -Ft. Vol. 28, pp. 309, 78, -Ft.

Monographs on the Radiochemistry of Elements: Sub-Committee on Radiochemistry, National Academy of Sciences, National Research Council, Washington, D.C. **The Radiochemistry of Manganese:** G. W. LEDDICOTE. NAS–NS–3018. October 1960. $0.50. **The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium:** P. C. STEVENSON and W. E. NERVIK. NAS–NS–3020. February 1961. $3.00. **The Radiochemistry of Technetium:** E. ANDERS. NAS–NS–3021. November 1960. $0.50. **The Radiochemistry of Tin:** W. E. NERVIK. NAS–NS–3023. October 1960. $0.75. **The Radiochemistry of Magnesium:** A. W. FAIRHALL. NAS–NS–3024. January 1961. $0.50. **The Radiochemistry of the Rare Gases:** F. F. MOMYER, JR. NAS–NS–3025. October 1960. $0.75. **The Radiochemistry of Mercury:** J. ROESMER and P. KRUGER. NAS–NS–3026. December 1960. $0.50. **The Radiochemistry of Copper:** F. F. DYER and G. W. LEDDICOTE. NAS–NS–3027. April 1961. $0.75. **The Radiochemistry of Rhenium:** G. W. LEDDICOTE. NAS–NS–3028. April 1961. $0.50.

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Talanta, 1961, Vol. 8, pp. 565 to 568. Pergamon Press Ltd. Printed in Northern Ireland

CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—VI*

THE MASKING OF TERVALENT CHROMIUM

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(*Received* 30 *January* 1961: *Accepted* 15 *February* 1961)

Summary—The conditions for the masking of tervalent chromium have been studied. Triethanolamine, ascorbic acid, and EDTA were used as screening reagents. It was found that ascorbic acid is the most convenient masking agent for chromium. Some new procedures for the determination of nickel, manganese, and calcium in the presence of chromium (iron and aluminium) are described. The suitability of all the proposed methods is discussed.

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THE selectivity of complexometric methods can be markedly increased by masking other accompanying elements. For this purpose a wide range of complex-forming reagents may be used, these being capable of forming with certain cations very stable and possibly soluble and colourless complexes, inactive towards EDTA as well as towards indicators. One of the first, potassium cyanide, was used to mask certain bivalent cations.[1] Subsequently triethanolamine was found to be suitable for masking iron and aluminium;[2] and BAL[3] or thioglycollic acid[4] for masking lead, copper, zinc, *etc.* Aluminium, and, at the same time, calcium and magnesium, are very often masked by ammonium fluoride.[5] Other masking reagents may be mentioned, such as thiourea for copper,[6] potassium iodide or thiosemicarbazide[7] for mercury, *etc.* A suitable combination of these reagents allows an extension of the possibilities of complexometry, especially in the routine analysis of alloys, ores, concentrates, *etc.*

Great difficulties arise in masking elements with small complex-forming tendency, or cations forming very intensely coloured complexes. Recently a method was developed for masking moderate concentrations of manganese.[8]

Likewise, the determination of chemically related cations, such as Co—Ni or Zn—Cd, is difficult because of the lack of specific masking reagents.

One of the elements for which no suitable masking agent has yet been found is tervalent chromium. It might be assumed that its transformation into chromate would be helpful in, for example, the determination of calcium, provided that the indicator used is sufficiently stable against oxidation by chromate. In solving this problem, one has to keep in mind the probable intense coloration of the complexes of tervalent chromium which are formed, since they probably would interfere at the end-point of the titration.

The behaviour of triethanolamine, ascorbic acid, and EDTA itself, as masking agents for chromium, has been examined. Experiments with these three reagents, together with the masking of chromium as chromate are described.

EXPERIMENTAL AND RESULTS

Reagents

EDTA solution, 0·05*M*, was prepared by dissolving 37·22 g of reagent-grade CHELATON 3 (Chemapol, Prague) and diluting to exactly 2 litres with distilled water. If necessary, the solution can

* Part V—Rudolf Přibil and Vladimír Veselý, *Talanta*, 1961, **8**, 270, 565.

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be standardised against lead nitrate by an EDTA titration, using Xylenol Orange as indicator.

Solutions of *iron chloride*, *calcium chloride*, *nickel nitrate*, *potassium chromium sulphate*, *manganese sulphate* (0·05*M*) and *potassium dichromate* (0·025*M*) were prepared by the usual methods and were standardised gravimetrically or by EDTA titration.

Indicator: Thymolphtalexon (Chemapol, Prague) in a triturated mixture with potassium nitrate in the ratio 1:100.

Other reagents, such as concentrated *triethanolamine*, *ascorbic acid*, and solutions of 1*M HCl* or HNO_3 and 1*M NaOH*, were also of reagent-grade purity.

1. *The masking of chromium with triethanolamine (TEA)*

The intensely red complex of tervalent chromium with triethanolamine is reliably formed under the following conditions: Not more than 30 ml of chromium salt solution are mixed with concentrated ammonia and then with concentrated triethanolamine. By boiling, previously precipitated chromium hydroxide dissolves in 5 min. A clear ruby red solution is obtained. The mixture of ammonia and TEA may be a single addition. TEA alone also precipitates chromium hydroxide but this dissolves after addition of ammonia only on prolonged boiling, and then slowly and not quantitatively. The presence of chromium hydroxide, even in milligram amounts, obscures the end-point detection when indicators such as Thymolphtalexon, methylthymol blue *etc.* are used. It is therefore necessary to work with the smallest possible volume, and reagents should be added in the order described.

With TEA, iron is also masked. In sufficiently alkaline solutions the Fe-TEA-complex is practically colourless. TEA also masks aluminium.

The Cr-TEA-complex, once formed, is quite stable, and its solution can be diluted to such an extent that the resulting colour does not interfere with the colour change of the indicator in a calcium titration. The proposed method was tested in the determination of calcium in synthetic mixtures of chromium, iron, aluminium and calcium.

Procedure: To 20–25 ml of slightly acid solution (in a 500- or 750-ml tall beaker) containing not more than 15 mg of iron or aluminium, 20–30 ml of concentrated ammonia and 10 ml of concentrated TEA, or alternatively a mixture of both reagents, are added. The whole is heated to boiling for 10 min. After cooling, EDTA solution in excess is added and the previously precipitated calcium carbonate is allowed to dissolve. (This takes perhaps about 30 min.) The solution is only slightly violet when sufficiently diluted with distilled water. If, after long boiling, the solution is not alkaline enough, a further 5–10 ml of concentrated ammonia, and then 0·1 g of indicator are added and the solution is titrated with 0·5*M* calcium chloride solution to a persistent blue-violet colour. The solution must be well stirred with a glass rod throughout the titration. The colour change is sufficiently sharp if the concentration of chromium does not exceed 40 mg in 500 ml of the titrated solution. Some results are given in Table I.

TABLE I.—MASKING OF CHROMIUM WITH TRIETHANOLAMINE. DETERMINATION OF CALCIUM.

Taken, *mg*		0·05*M* EDTA, *ml*	0·05*M* $CaCl_2$, *ml*	Ca found, *mg*	Difference, *mg*
Cr	Ca				
26·00	10·04	5·96	0·96	10·01	−0·03
2·60	20·08	11·92	1·95	19·96	−0·12
13·00	40·14	24·82	4·93	39·87	−0·20
29·00	2·00	4·96	3·91	2·11	0·11
5·20	2·00	1·98	0·96	2·05	0·05
2·60	10·04	9·93	4·96	9·96	−0·08
2·60	4·01	9·93	7·99	3·88	−0·13

2. *The masking of chromium with ascorbic acid*

The solution of the chromium salt, in the presence of ascorbic acid, is precipitated with ammonia. After sufficient boiling, an apparently stable complex of tervalent chromium is formed. Such solutions

do not react further with ammonia, neither do they interfere with the indicators used. The colour, which is bluish-green, is relatively weak so that 50 mg of chromium in 500 ml have no influence on the colour change of the indicator. This method of masking can be used for the determination of calcium, manganese or nickel in the presence of chromium.

Procedure: To 50–100 ml of slightly acid solution 1–2 g of ascorbic acid are added and the whole is boiled for 10–15 min. After cooling, a known amount of EDTA in excess is added, followed by 10 ml of concentrated ammonia and 0·1 g of indicator mixture. The solution is titrated with 0·05*M* calcium chloride to an intense blue colour. Some results are summarised in Table II.

TABLE II.—MASKING OF CHROMIUM WITH ASCORBIC ACID. DETERMINATION OF CALCIUM, MANGANESE OR NICKEL.

Taken, *mg*		0·05M EDTA, *ml*	0·05*M* $CaCl_2$, *ml*	Metal found, *mg*	Difference, *mg*
Cr	Metal				
2·60	2·00 Ca	1·99	1·00	1·98	−0·02
26·00	2·00	4·97	3·99	1·96	−0·04
2·60	40·16	21·84	1·89	39·99	−0·17
52·01	2·00	9·93	8·94	1·98	−0·02[a]
13·00	10·04	5·96	0·94	10·06	0·02
26·00	20·08	11·92	1·92	20·04	−0·04
2·66	2·61 Mn	4·99	4·05	2·57	−0·04
5·33	26·07	14·95	5·46	25·91	−0·16
26·62	52·14	24·92	5·82	52·46	0·32
2·66	2·93 Ni	1·99	0·98	2·97	0·04
53·25	5·87	4·99	2·97	5·93	0·06
13·32	44·02	24.92	9·92	44·05	0·03

[a] Diluted to 500 ml before titration.

Note: In this procedure it is necessary to add the EDTA before the ammonia, otherwise a precipitate, which dissolves in EDTA very slowly, is formed. At higher concentrations of chromium it is advisable to dilute the solution to a suitable volume before titration.

3. *The masking of chromium with EDTA*

Chromium in slightly acid solutions (pH 1–2) forms with EDTA, by boiling for 10–15 min, an intensely red-violet 1:1 complex. In alkaline medium the solutions turn to light blue, because of the formation of the hydroxo-complex $CrY(OH)_2^{3-}$. In these solutions, after sufficient dilution, it is possible to titrate the excess of EDTA with calcium chloride, using Thymolphtalexon as indicator, provided that the concentration of chromium does not exceed 2·5 mg in 100 ml. Under the same conditions, certain other cations, together with chromium can be determined. Separate determination is possible only in the case of elements which can be masked by other complex forming reagents: *e.g.*, after addition of potassium cyanide, nickel can be determined indirectly. Some results of the analysis of nickel-chromium alloys have already been published.[9]

4. *Masking of chromium as chromate*

Light yellow solutions of chromate containing up to 12 mg of Cr in 100 ml have no effect on the colour change of Thymolphtalexon or methylthymol blue. Eriochrome Black T in chromate solutions slowly decomposes after 10 minutes, and the end-point detection fails. With the first two indicators the yellow colour changes to green at the end-point. Higher concentrations of indicator improve the sharpness of the colour change. In this procedure it is possible to use TEA to mask iron and aluminium. This method has been applied in the analysis of Fe-Cr-Ni alloys.[10]

DISCUSSION

From those methods for masking tervalent chromium so far studied, the complexation with ascorbic acid is the most suitable. This procedure is simple and more

reliable than *e.g.* masking with triethanolamine. The emerald-green complex which is formed by boiling the slightly acid solutions of chromium with excess of ascorbic acid does not interfere in the subsequent complexometric titration, provided that the concentration of Chromium does not exceed 50–55 mg in 500 ml of the titrated solution. Likewise, a high concentration of ascorbic acid has no effect on the colour change of the indicators. The use of other complex-forming reagents such as triethanolamine or potassium cyanide, after complexation of chromium, offers further possibilities; for example, a rapid determination of nickel, manganese or calcium in the presence of chromium, aluminium and iron may be carried out. The whole problem is being further studied from the point of view of practical utilisation.

Zusammenfassung—Die Bedingungen zur Maskierung von dreiwertigem Chrom wurden studiert Triäthanolamin, Ascorbinsäure und ÄDTA werden als Maskierungsmittel verwendet. Ascorbinsäure wird als das beste Reagens erachtet. Einige neue Methoden zur Bestimmung von Nickel, Mangan und Calcium in Gegenwart von Chrom (Eisen und Aluminium) werden beschrieben. Verwendungsfähigkeit der vorgschlagenen Methoden werden diskutiert.

Résumé—Les auteurs ont étudié les conditions nécessaires pour complexer le chrome trivalent. La triethanolamine, l'acide ascorbique et l'EDTA ont été utilisés comme agents complexants: l'acide ascorbique s'est révélé le plus commode. De nouvelles méthodes de dosage du nickel, du manganèse et du calcium en présence de chrome (fer et aluminium) ont été décrites. L'intérêt de toutes les méthodes proposées est discuté.

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[4] R. Přibil and V. Veselý, unpublished results.
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[9] R. Přibil and V. Veselý, *Chemist-Analyst*, in press.
[10] *Idem*, *ibid.*, In the press.

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THE DISTRIBUTION OF VANADIUM BETWEEN ALCOHOLIC- HYDROCHLORIC ACID SOLUTIONS AND THE STRONGLY BASIC ANION-EXCHANGER DOWEX—1

SEPARATION OF VANADIUM AND NICKEL FROM IRON AND COPPER

G. E. JANAUER and J. KORKISCH
Analytical Institute of the University of Vienna, Austria

(*Received* 28 *January* 1961; *Accepted* 26 *February* 1961)

Summary—The present work was designed to furnish data about the adsorption behaviour of vanadium in alcohols of the aliphatic series, employing the strongly basic anion-exchanger Dowex-1, X8 as an adsorbent. The distribution coefficients for vanadium have been determined in hydrochloric acid solutions containing varying amounts of alcohols of the aliphatic series. In addition, some distribution coefficients for nickel, iron and copper were determined. Based on these results, a method for the separation of vanadium and nickel from iron and copper by means of a column operation was developed.

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EXPERIMENTS carried out by Kraus, Nelson and Smith[1] showed that vanadium is only very weakly retained from hydrochloric acid solutions on strongly basic anion-exchangers, which means that the tendency of vanadium to form negatively charged chloride complexes is rather low. We therefore have tried to apply here the same principle which has been used earlier[2–5] with uranium, thorium, zirconium and titanium *i.e.*, application of the stabilising effect of organic solvents (alcohols) on the inorganic complexes of these elements. As can be seen from the experimental results recorded in this paper, the distribution coefficients of vanadium, and hence the stability of its chloride complexes even in alcoholic media, are rather low, except at very high alcohol concentrations, especially in the iso-alcohols. In general, the distribution coefficients increased with increasing chain length of the alcohols examined. Since nickel shows nearly the same adsorption behaviour as vanadium, whereas copper and iron have, under the same conditions, much higher distribution coefficients, the separation of these two pairs of ions from each other was possible.

EXPERIMENTAL

Solutions and reagents

For the determination of the distribution coefficients in mixed hydrochloric acid-alcohol solutions, the air-dried, strongly basic anion-exchanger, Dowex-1, X8 (100–200 mesh, chloride form) was used. Solutions of 1–12*N* hydrochloric acid, and a number of aliphatic alcohols, *viz.* methanol, ethanol (95% ethanol containing 5% of gasoline is arbitrarily taken as 100% ethanol), n-propanol, n-butanol, isopropanol, isobutanol, ethylene glycol, all chemically pure, were employed.

Vanadium^{V} solutions were obtained by dilution of a spectrophotometrically tested standard vanadate solution prepared from a weighed amount of ammonium metavanadate r.g. (Merck), and 0·005*N* hydrochloric acid. Ascorbic acid r.g. (Wiener Heilmittelwerke) was used to reduce vanadium to the quadrivalent state.

Standard solutions of nickel, copper and iron were prepared by dissolving weighed amounts of the r.g. chlorides of these elements in hydrochloric acid of suitable normality.

The amount of the elements present in solution was determined spectrophotometrically.[6–10] Vanadium was determined quantitatively with Solochrome Fast Grey* (0·01% aqueous solution)[6,7] using a Beckman model B spectrophotometer. The absorbance measurements were carried out in 1-cm cells, at 560 mμ, using a blue-sensitive photo-tube. The column operations were carried out in columns of the same type and dimensions as described earlier.[11]

Quantitative determination of vanadium, nickel, copper and iron. Determination of vanadium

Vanadium determinations in the effluents, or in the filtrates after removing the resin, were carried out in the following manner. An aliquot was transferred to a quartz dish, and the solution was evaporated to dryness on a water bath. The residue was then ignited to destroy organic matter. After cooling to room temperature, 5 ml of 6*N* hydrochloric acid were added, and the solution was evaporated to dryness once more. The residue was then taken up in 1 ml of 0·1*N* hydrochloric acid, and 2 ml of distilled water were added. After transferring this solution to a 10-ml measuring flask, using 3 ml of distilled water, 3·5 ml of the dyestuff solution were added. To this solution 0·1 ml of a 7% aqueous ascorbic acid solution and 0·1 ml of a 2*M* ammonium thiocyanate solution were added and the flask was made up to volume with distilled water. The absorbance of this solution was then measured against a reagent blank at 560 mμ.[6,7]

Determination of nickel, copper and iron

The methods used for the quantitative determination of nickel and copper were exactly the same as those described in earlier papers.[8–10] Iron was determined by means of the standard procedure using sulphosalicylic acid in ammoniacal medium.[10]

Determination of distribution coefficients

The distribution coefficient, K_d is defined by the equation

$$K_d = \frac{\mu\text{g of element/g of resin}}{\mu\text{g of element/ml of solution}}$$

as shown in earlier papers.[2–5] Weighed amounts of the air-dried resin (mostly 1 g) were added to the alcoholic-hydrochloric acid mixtures containing the element in question (usually 1 mg in 20 ml of the mixture) and agitated mechanically for 24 hr. The resin was then filtered off, and the vanadium, nickel, *etc.*, were determined in the filtrate as described above. The results shown in Figs. 1–3 and Table 1 were obtained using this procedure.

Column operations: separation of vanadium and nickel from iron and copper

The air-dried resin was soaked in an alcohol-hydrochloric acid mixture of the same composition as that used for the column operation (see Table II) and then—carefully avoiding the introduction of air bubbles—was filled into the column, which already contained the same solution. The resin bed was sealed at both ends by small pads of glass wool, and was pretreated with 50 ml of the mixture. The mixture (see Table II) containing the ions under investigation, which had previously been allowed to stand for about 6 hr, was then passed through the column at a flow-rate of about 0·5 ml/min. Normally 100 ml of the mixture were used for the sorption step. After sorption, the column was washed once with 10 ml and a second time with 5 ml of the mixture which was used for sorption and pretreatment of the resin bed. After this operation vanadium and nickel are to be found quantitatively in the effluent whereas copper and iron are retained by the resin. These two elements can easily be removed from the exchanger by elution with 1*N* hydrochloric acid. Results are given in Table II.

RESULTS

Fig. 1 shows the effect of the alcohol concentration on the distribution coefficient of vanadium.

* Imperial Chemical Industries, Ltd., Hexagon House, Blackley, Manchester, 9, England.

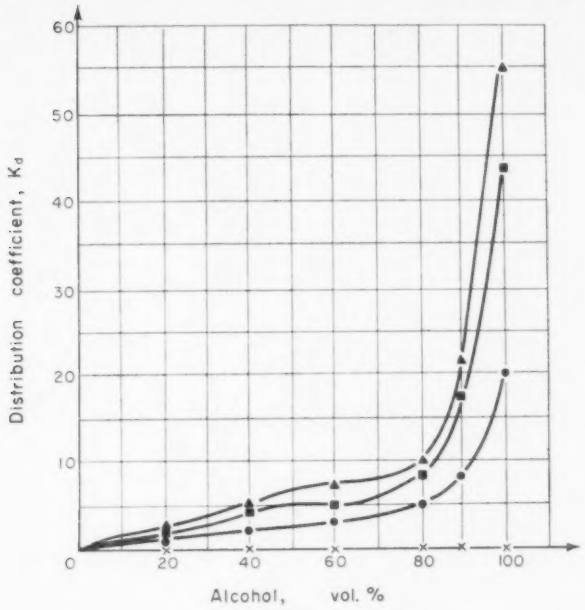

FIG. 1.
× methanol
● ethanol
■ n-propanol
▲ n-butanol

The curves show that the adsorption of vanadium on the resin is highest in a butanolic and lowest in a methanolic medium. By using 1, 6 and 12*N* hydrochloric acid, identical curves were obtained. In branched chain and multivalent alcohols the distribution coefficient is much higher, as can be seen from the results recorded in Table I, which also shows the distribution coefficients of copper, nickel and iron in a 10:90 (V:V) 6*N* hydrochloric acid:methanol mixture, which proved to be most suitable for the separation of vanadium and nickel from iron and copper.

TABLE I.

Ion used	Normality of acid	HCl:ROH ratio	ROH	K_d
V^{V}	1–12	1:99	isopropanol	238
V^{V}	1–12	1:99	isobutanol	246
V^{V}	1–12	1:99	ethylene glycol	200
V^{V}	6	10:90	methanol	<1
Ni	6	10:90	methanol	<1
Cu	6	10:90	methanol	148
Fe^{III}	6	10:90	methanol	485

To show the effect of the chain length of the n-alcohols on the adsorption of vanadium^{V} and vanadium^{IV}, the distribution coefficients of vanadium in 6*N* hydrochloric acid (1%):alcohol (99%) mixture were plotted against the chain length (see Fig. 2).

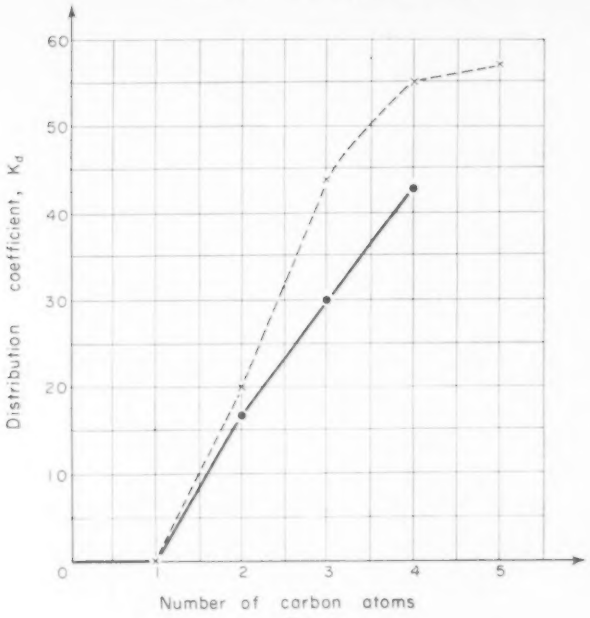

FIG. 2.
—— vanadium^{IV}
– – – vanadium^{V}

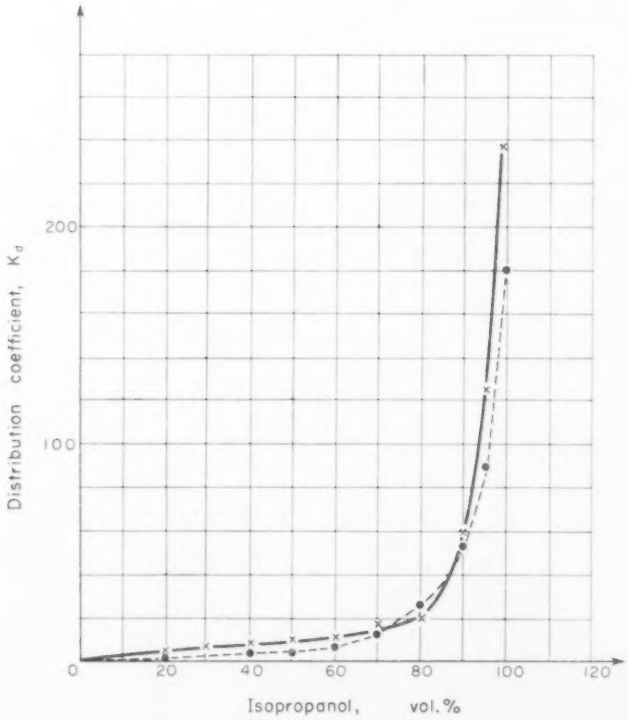

FIG. 3.
——— vanadium (1-12*N* hydrochloric acid)
– – – – nickel (12*N* hydrochloric acid)

From this it is evident that the distribution coefficients of quinque- and quadrivalent vanadium increase almost linearly up to n-butyl alcohol. Since the isopropyl and isobutyl alcohols proved to give the highest distribution coefficients (see Table I), the adsorption behaviour of vanadium^{V} in isopropanol-hydrochloric acid (I–12*N*) mixtures of varying percentages was examined. The results of these experiments are shown in Fig. 3.

The curve for vanadium in Fig. 3 holds for the entire pH-range from 1–12*N* hydrochloric acid. Nickel in mixtures of 12*N* hydrochloric acid-isopropanol shows a slightly smaller adsorption (see dotted lines in Fig. 3). The origin of the co-ordinate system in this figure as well as in Figs. 1–2 corresponds to 100% aqueous phase *i.e.*, hydrochloric acid of the normality stated for the mixtures. (Fig. 1, 1, 6, and 12*N*; Fig. 2, 6*N*; Fig. 3, 1–12*N*).

Separation of vanadium and nickel from copper and iron

Table II records the results of a series of experiments which show that the separation of vanadium and nickel from small amounts of copper and larger amounts of iron is quantitative, as expected from the distribution coefficients given above. Since the distribution coefficient of copper in the mixture used for the column operation *i.e.*, 90:10 methanol:6*N* hydrochloric acid, is not very high (see Table I), quantitative separation from copper is only possible if relatively small amounts (up to a ten-fold amount in respect of vanadium or nickel in the microgram range) are present; whereas iron may be tolerated up to milligram amounts.

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TABLE II.

Normality of hydrochloric acid	Mixture		Amounts used, *μg*				Amounts recovered, *μg* (effluent)			
	Hydrochloric acid, %	Methanol, %	V	Ni	Cu	Fe	V	Ni	Cu	Fe
6	20	80	10	10	10	10·000	10	10	5	0
6	15	85	10	10	10	10·000	10	10	2	0
6	10	90	10	10	10	10·000	10	10	0	0
6	10	90	10	10	100	10·000	10	12	2·5	0
12	10	90	10	10	10	10·000	10	14·3	5·7	0
6	5	95	10	10	10	10·000	10	9·5	0	0

An application of this separation method has proved to be suitable for the determination of vanadium and nickel in ashes of oil products.[12]

Zusammenfassung—In der vorliegenden Arbeit wird das Adsorptionsverhalten von Vanadium am stark basischen Anionenaustauscher Dowex 1 in Mischungen von Salzsäure und aliphatischen Alkoholen beschrieben. Verteilungskoefficienten für Vanadium, Nickel, Kupfer und Eisen werden angegeben. Diese Resultate dienen als Grundlage fur eine Trennung der Elemente Vanadium und Nickel von Kupfer und Eisen mittels einer Säulenoperation.

Résumé—Les auteurs donnent des résultats sur l'adsorption du vanadium dans les alcools de la série aliphatique, en utilisant comme adsorbant la résine échangeur d'anions Dowex-1, ×8 fortement basique. Les coefficients de partage du vanadium ont été déterminés dans des solutions d'acide chlorhydrique contenant différentes concentrations d'alcools de la série aliphatique. Les coefficients

de partage du nickel, du fer et du cuivre ont été déterminés ultérieurement. D'après ces résultats, une méthode de séparation du vanadium et du nickel d'une part, du fer et du cuivre d'autre part, au moyen d'une opération sur colonne, a été mise au point.

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DETERMINATION OF RADIOPHOSPHORUS BY SOLVENT-EXTRACTION

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Summary—A procedure is given for the determination of radiophosphorus in the presence of other activities. Potassium phosphate is added as carrier and the phosphorus is extracted as phosphomolybdic acid into a butanol-chloroform mixture. The activity is back-extracted into ammonium hydroxide and the phosphate is precipitated as magnesium ammonium phosphate. This may be air-dried or ignited to magnesium pyrophosphate for counting.

The method is rapid, accurate, and free from interference by other radionuclides. Especially noteworthy is the excellent separation from radioarsenic.

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THE radioactive isotope of phosphorus, ^{32}P, is widely used as a tracer in chemical, medical and industrial research. It is also found as a neutron-activated by-product in nuclear reactor coolant systems. Phosphorus-32 is a pure β-emitter having a maximum energy of 1·701 MeV and a half-life of 14·01 days.[2] The following paper describes a new method for the determination of ^{32}P in the presence of fission products and other radionuclides. Arsenic-76, a common contaminant of phosphorus-32, does not interfere.

A method for the determination of phosphorus-32 was developed by Bonner and Potratz.[1] Their procedure involves the precipitation of phosphorus as zirconium phosphate, and later as ammonium phosphomolybdate. Arsenic is removed by the precipitation of arsenic pentasulphide. A lanthanum fluoride scavenging step is also included. Phosphorus is finally precipitated as magnesium ammonium phosphate, in which form it is counted. This method is quite involved and a single analysis requires about 7 hours.

Silker[4] developed a rapid procedure for the separation and determination of phosphorus. In his method, arsenic is separated from phosphorus first by reducing the arsenic with sodium thiosulphate, then passing the resulting solution through a copper^{II} sulphide bed, which retains 98·5% of the arsenic. The effluent is subjected to a solvent-extraction procedure, and an aliquot of the organic phase is evaporated on a planchet and counted. This method is unsatisfactory in three respects: it is an empirical procedure and no correction is made for carrier loss; about 1·5% of the arsenic is carried with the phosphorus and is not removed in the solvent extraction step. Since only an aliquot of the sample is counted, there is a loss of accuracy in low-level samples. Several known samples were analysed in our laboratory using this method and the results were found to be erratic and unreliable.

Other methods for the determination of radiophosphorus have been published, but these usually involve the counting of the phosphorus in samples free from other radiochemical interference or involve some modification of the Bonner and Potratz procedure for a specialised sample.

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Previous studies[3] suggested that a direct solvent-extraction procedure could be used for the separation of radiophosphorus. From this work a method was developed which is rapid, accurate, and free of interference from other radionuclides. The procedure requires no special laboratory equipment and is suitable for the determination of radiophosphorus where small volumes of sample material (up to 5 ml) will give a significant activity.

EXPERIMENTAL

Reagents

In addition to standard laboratory reagents, the following solutions were required:

Phosphorus carrier: Dissolve 2·8657 g of pure, dry potassium dihydrogen phosphate in 100 ml of water and dilute to 1 litre. The resulting solution contains 2·00 mg of PO_4^{-3} per ml.

Sodium molybdate, 20%: Dissolve 200 g of $Na_2MoO_4 \cdot 2H_2O$ in water to make 1 litre.

Potassium permanganate, 0·5*M*: Dissolve 8 g of $KMnO_4$ in 100 ml of water.

Magnesia mixture: Dissolve 55 g of magnesium chloride and 140 g of ammonium chloride in 500 ml of water. Add 130 ml of concentrated ammonium hydroxide and dilute to 1 litre.

Tracer solutions: Tracer solutions of phosphorus-32, arsenic-76, strontium-yttrium-90, cobalt-60, iridium-192, cerium-144, thallium-204, hafnium-181, ruthenium-106, zinc-65, zirconium-niobium-95, molybdenum-99, and iodine-131 from the Isotopes Division, Oak Ridge National Laboratory, were diluted to the desired activity before use.

Niobium-95: A tracer solution of niobium-95 was prepared by extracting the zirconium-95 activity from a solution of the mixed isotopes with 0·5*M* thenoyl trifluoroacetone (TTA) in xylene. The extraction was done in 0·2*N* hydrochloric acid, yielding an aqueous solution free of the zirconium isotope.

10% Butanol-chloroform: Dilute 100 ml of 1-butanol (*n*-butyl alcohol) with 900 ml of chloroform.

Procedure

1. Pipette 1–5 ml of sample into a 40-ml centrifuge tube, then add 5 ml of phosphate carrier (10 mg of PO_4^{-3}).
2. Add 5 ml of 72% perchloric acid, mix, then heat to boiling. (If chlorides, bromides, iodides or other reducing agents are present, the solution should be evaporated to fumes of perchloric acid to eliminate these ions, then diluted back to about 10 ml).
3. Add 5–8 drops of 0·5*M* potassium permanganate solution and continue heating until the permanganate colour is discharged and a precipitate of manganese dioxide is formed.
4. Centrifuge down the manganese dioxide precipitate and decant the supernate to a 250-ml separatory funnel.
5. Cool, then add 40 ml of 10% butanol-chloroform solvent.
6. Add 15 ml of concentrated hydrochloric acid and 20 ml of a 20% sodium molybdate solution, stopper the funnel, shake for 2 min, and allow the layers to separate, then drain lower the organic layer into another 250-ml separatory funnel.
7. Prepare a solution by adding 5 ml of water, 15 ml of 20% sodium molybdate solution, and 20 ml of concentrated hydrochloric acid to a 50-ml beaker. Add this solution to the solution in the separatory funnel of step (6).
8. Shake the separatory funnel for 2 min and allow the layers to separate. Drain the lower organic layer to a third 250-ml separatory funnel.
9. Add 50 ml of a 3*M* ammonium hydroxide-1*M* ammonium chloride buffer solution to the third funnel, shake for 2 min, allow the layers to separate, drain the lower layer into a waste jar, and transfer the aqueous layer into a 100-ml beaker.
10. Heat the solution in the beaker to boiling, add 10 ml of magnesia mixture, then allow to cool (15 min).
11. Collect the precipitate on a filter disc in a Hirsh funnel. Wash the precipitate with three 10-ml portions of buffer solution and three 5-ml portions of acetone.
12. For ordinary accuracy follow step (13a). For highest accuracy follow step (13b).

13a. Air-dry the precipitate for 5 min and weigh. Subtract the weight of the filter disc to obtain the weight of the precipitate. Transfer to a watch glass, β-count, and correct for gravimetric yield.

13b. Transfer the precipitate on the disc to a crucible and ignite at red heat for 1 hr. Cool, transfer the precipitate to a watch glass, weigh, β-count, and correct for gravimetric yield.

RESULTS

The above procedure was tested using samples of distilled water with added phosphorus activity. The count was made on two forms of the final precipitate, magnesium ammonium phosphate, and magnesium pyrophosphate obtained by ignition of the former. Six samples were run and the results are shown in Table I.

TABLE I.—RECOVERIES OF PHOSPHORUS-32 USING 10% BUTANOL-CHLOROFORM SOLVENT AND 10 mg OF PHOSPHATE CARRIER

Sample	Activity added, *cpm*	Activity recovered*		% Error	
		not ignited	*ignited*	*not ignited*	*ignited*
1	9,473	9,338	9,445	−1·43	−0·30
2	9,473	9,287	9,447	−1·96	−0·27
3	9,473	9,481	9,446	+0·08	−0·28
4	9,473	9,304	9,461	−1·78	−0·13
5	9,473	9,223	9,450	−2·64	−0.21
6	9,473	9,292	9,447	−1·91	−0·27
average				−1·61	−0·24

* Corrected for gravimetric yield.

TABLE II.—PERCENT ARSENIC-76 EXTRACTED USING 10% BUTANOL-CHLOROFORM SOLVENT AND 10 mg OF PHOSPHATE CARRIER

Sample	Counts added, *cpm*	Counts recovered* *cpm*	% Extracted
1	482,820	20	0·0041
2	482,820	25	0·0052
3	482,820	18	0·0038
4	377,490	15	0·0031
5	377,490	20	0·0042
6	377,490	16	0·0033
average			0·0039

* Corrected for gravimetric yield.

All gravimetric yields for the six samples fell in the range of 71 to 76%. This was true for both the ignited and non-ignited forms.

The extent of arsenic interference was determined using the same procedure, except that arsenic tracer was added in place of phosphorus-32. Table II shows results from these samples. Gravimetric yields ranged from 70 to 76%.

Several other isotopes were examined (about 50,000 cpm each of strontium-90, cobalt-60, iridium-192, cerium-144, thallium-204, ruthenium-106, zinc-65, molybdenum-99, hafnium-181, zirconium-niobium-95, and niobium-95) to determine the extent of their interference in the radiometric determination of phosphorus. The same

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procedure was used, except that the isotope being investigated was substituted for the radiophosphorus. None of the isotopes interfered.

The manganese dioxide scavenging (steps 3 and 4) is necessary to remove radioniobium which is extracted with phosphorus and carried along to the final precipitate. If this activity is definitely known to be absent, steps 3 and 4 may be omitted.

Zusammenfassung—Eine Methode zur Bestimmung von Radio-Phosphor in Gegenwart anderer Aktivitäten wird beschrieben. Kaliumphosphat wird als Träger zugesetzt und der Phosphor als Phosphomolybdänsäure mit Butanol-Chloroform ausgezogen. Die Aktivität wird mittels Ammoniak rückextrahiert und das Phosphat als Magnesiumsalz gefällt. Dieses kann luftgetrocknet oder zu Pyrophosphat verglüht und dann gezählt werden. Die Methode ist rasch, genau und frei von Störungen durch andere Aktivitäten. Besonders bemerkenswert ist die ausgezeichnete Trennung von radioaktivem Arsen.

Résumé—Les auteurs présentent une méthode de dosage du radiophosphore en présence d'autres composés radioactifs. Du phosphate de potassium est ajouté comme entraîneur, le phosphore est extrait à l'état d'acide phosphomolybdique dans un mélange butanol-chloroforme. Le composé est activé et extrait à nouveau par de l'ammoniaque, et le phosphate est précipité à l'état de phosphate ammoniaco-magnésien. Celui-ci peut être séché à l'air, ou calciné en pyrophosphate de magnésium pour être compté. La méthode est rapide, précise et n'est pas gênée par les autres radio-éléments. La séparation excellente du radio-arsenic est spécialement intéressante.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—IV

URANIUM

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Summary—Uranium^{VI} 8-hydroxyquinolate can be precipitated from homogeneous solution with 8-hydroyxquinoline generated by the hydrolysis of 8-acetoxyquinoline. The composition of the uranium chelate formed is not the same for the two procedures described for the quantitative precipitation of the uranium.

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8-ACETOXYQUINOLINE can be hydrolysed to produce 8-hydroxyquinoline and thus to precipitate metallic ions from homogeneous solution.[1–4] The present paper describes an analogous method for the precipitation of uranium^{VI}. Two procedures have been developed. In one procedure the uranium is precipitated at pH 6.8 as $(UO_2Q_2)_2 \cdot HQ$, where $Q = C_9H_6NO$; and in the other procedure at pH 5.0 as $UO_2Q_2 \cdot HQ$. The compound which is precipitated upon the conventional addition of 8-hydroxyquinoline to a uranium^{VI} solution is $UO_2Q_2 \cdot HQ$.[5,6]

EXPERIMENTAL

Procedure

(1) *Precipitation at* pH 6.8*:* Dissolve 100 mg of pure 8-acetoxyquinoline in 45 ml of 1 : 1 acetic acid. Add to this a solution containing 5–30 mg of uranium, and dilute to 100 ml. Adjust the pH to 6.8 with concentrated ammonium hydroxide, and heat the solution at 70° for 3 hr. Cool, filter, and wash the precipitate with a minimum of cold distilled water. Dry the precipitate for 2 hours at 110°. Use the conversion factor, $2U/(UO_2Q_2)_2 \cdot HQ = 0.3773$, to calculate the uranium content of the precipitate.

(2) *Precipitation at* pH 5.0*:* Dissolve 1.0 g of pure 8-acetoxyquinoline in 10 ml of 1 : 1 acetic acid. Add to this a solution containing 5–60 mg of uranium, and dilute to 100 ml. Adjust the pH to 5.0 using ammonium hydroxide (1 : 1) and heat for 3 hr at 70°. Cool, filter, and wash with a minimum of cold distilled water. Dry the precipitate for 2 hr at 110°. Use the conversion factor, $U/UO_2Q_2 \cdot HQ = 0.3384$, to calculate the uranium content of the precipitate.

Reagents

Uranium: Approximately 5 g of reagent grade $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ (Baker and Adams, New York) was dissolved in 5 litres of distilled water. The solution was standardised by evaporation of a known aliquot and ignition to U_3O_8, and this was checked by precipitation of the uranium with ammonium hydroxide followed by ignition to U_3O_8.

8-*Hydroxyquinoline:* The solution used was prepared by dissolving 3 g of the reagent (Matheson, Coleman, and Bell Division of the Matheson Company, East Rutherford, New Jersey) in 3 ml of glacial acetic acid, and diluting with hot water to 100 ml.

8-*Acetoxyquinoline:* This reagent was prepared by the method of Salesin and Gordon.[1] A few precipitations were effected with experimental quantities of 8-acetoxyquinoline obtained from the Burdick and Jackson Laboratories, Muskegon, Michigan. In these instances, the reagent was used as an acetone solution.

Preliminary investigations

Preliminary investigations were undertaken to determine the optimum pH, concentration, and temperature for quantitative reaction, and to obtain a precipitate with desirable physical characteristics.

A suitable temperature for the reaction was found to be 70°. Two concentrations of 8-acetoxyquinoline were used. When twice the stoichiometric quantity of 8-acetoxyquinoline was used to precipitate 28.0 mg of uranium (assuming the precipitate to be $UO_2Q_2 \cdot HQ$), no precititate formed below pH 5.5; precipitation began immediately above pH 7.5. Crystals with excellent characteristics formed at pH 6.8. When 20 times the stoichiometric quantity of 8-acetoxyquinoline was used to precipitate 28.0 mg of uranium (assuming the precipitate to be $UO_2Q_2 \cdot HQ$), quantitative precipitation of crystals with excellent characteristics occurred at pH 5.0. In both cases, precipitation occurred within 15 min and was quantitative after heating at 70° for 3 hr.

The precipitate obtained at pH 6.8 was reddish-orange whereas the precipitate obtained at pH 5.0 appeared dark red; when viewed under the microscope with transmitted light, the precipitate obtained at pH 5.0 appeared yellow.

The precipitates obtained by PFHS (precipitation from homogeneous solution) are superior in physical characteristics to those obtained by conventional precipitation. Quantitative precipitation of the uranium is effected by both procedures (*cf.* Tables I, and II).

TABLE I.—PRECIPITATION OF URANIUM AT pH 6·8

Method of precipitation	Conventional[a]	PFHS[b]	PFHS	PFHS	PFHS[c]
Diverse ion taken *mg*	None	None	Ca, 4.7	Mg, 2.8	Pb, 24.4
Uranium taken, *mg*	28.0	28.0	28.0	28.0	28.0
Difference in uranium found, *mg*					
I. Calc. on basis of $UO_2Q_2 \cdot HQ$	0.0, −0.1, 0.0	−3.1, −3.0, −3.0, −2.9, −2.9, −2.9	—	—	—
II. Calc. on basis of $(UO_2Q_2)_2 \cdot HQ$	+3.2, +3.1, +3.2	−0.2, −0.1, −0.1, 0.0, 0.0, 0.0	+2.9	+0.7	—

[a] Precipitated by method of Hecht and Reigh–Rohrwig.[5]
[b] Uranium in one of the filtrates determined by method of Francois[8] and found to be 0.12 mg.
[c] The precipitate which formed subsequently dissolved.

TABLE II.—PRECIPITATION OF URANIUM FROM HOMOGENEOUS SOLUTION AT pH 5·0

Diverse ion taken, *mg*	None	None	None[a]	None	Pb, 24.4	Mg, 2.8
Uranium taken, *mg*	5.6	14.0	28.0	56.0	28.0	2.80
Difference in uranium found, *mg*						
I. Calc. on basis of $UO_2Q_2 \cdot HQ$	−0.1	0.0	0.0, 0.0, 0.0	0.0	0.0, 0.0[b], 0.0[b]	0.0, 0.0, 0.0[b]
II. Calc. on basis of $(UO_2Q_2)_2 \cdot HQ$	+0.5	+1.5	+3.2, +3.2, +3.2	+6.1	—	—

[a] Uranium in one of the filtrates determined by method of Francois[8] and found to be 0.10 mg.
[b] The 8-acetoxyquinoline used in the determination was dissolved in 3 ml of acetone before addition of 10 ml of 1:1 acetic acid solution.

RESULTS AND DISCUSSION

(*a*) *Precipitation at* pH 6.8

The gravimetric results obtained in this investigation are summarised in Table I. The calculations indicate that the uranium is precipitated with a molecule of crystallization of 8-hydroxyquinoline, *i.e.*, with the formula $(UO_2Q_2)_2 \cdot HQ$. When the conventional method of precipitation with 8-hydroxyquinoline was used, the uranium

compound appeared to be $UO_2Q_2 \cdot HQ$, as has been previously reported.[5,6] Determination of the 8-hydroxyquinoline content of several of the precipitates by a bromination procedure[7] and comparison with the uranium content confirmed the assumed formulas as is shown in Table III.

TABLE III.—COMPOSITION OF URANIUM 8-HYDROXYQUINOLATES OBTAINED BY DIFFERENT METHODS OF PRECIPITATION

Method of precipitation	Conventional	PFHS at pH 6.8	PFHS at pH 5.0
Uranium taken, *moles*	0.000117	0.000117	0.000117
8-Hydroxyquinoline found, *moles*	0.000350	0.000288, 0·000289	0.000354, 0.000355, 0.000355
Molar ratio found for $\frac{HQ}{U}$	2.99	2.46, 2.47	3.03, 3.03, 3.03
Theory for $(UO_2Q_2)_2 \cdot HQ$	2.50	2.50	2.50
Theory for $UO_2Q_2 \cdot HQ$	3.00	3.00	3.00

Samples of the compound, $(UO_2Q_2)_2 \cdot HQ$, were dried for 60-min periods at various temperatures and then weighed to ascertain their thermal stability. As shown in Table IV, the precipitable is stable at 110° but slowly loses weight above 120°. At 180° it appears that the molecule of crystallisation is completely removed; above 180°, the compound is unstable.

TABLE IV.—EFFECT OF DRYING TEMPERATURE ON URANIUM 8-HYDROXYQUINOLATE OBTAINED BY PFHS AT pH 6.8

Uranium taken, *mg*	28.0							
Difference in uranium found[a], *mg*	−0.1	−0.4	−0.5	−0.6	−0.6	−0.6	−0.7	−3.3[b]
Temperature, °C	110	120	130	140	150	160	170	180

[a] Formula used as basis of calculation: $(UO_2Q_2)_2 \cdot HQ$.
[b] If compound is assumed to be UO_2Q_2 at 180°, then "difference mg" is 0.1 thus indicating complete loss of molecule of crystallisation.

Separation of uranium from calcium, magnesium, and lead was unsuccessful at pH 6·8, as is shown in Table I.

(*b*) *Precipitation at* pH 5.0

Gravimetric results obtained at pH 5.0 are shown in Table II. The composition of the compound obtained at this pH was confirmed by the bromination procedures; the results are shown in Table III.

The compound, $UO_2Q_2 \cdot HQ$, is stable at 110°; the effect of higher temperatures was not investigated.

In contrast to the results obtained at pH 6.8, separation of uranium from lead and magnesium at pH 5.0 was successful (a separation from calcium was not attempted).

Acknowledgment—The authors acknowledge the assistance of the United States Atomic Energy Commission in supporting in part the investigation reported herein under Contract AT(11–1)–582.

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Zusammenfassung—Uranium(VI)-oxinat wird aus homogener Lösung gefällt durch Hydrolyse von 8-Acetoxychinolin. Der so gewonnene Niederschlag hat eine andere Zusammensetzung als Niederschläge, die nach den beiden bekannten Mothoden zur Uranbestimmung erhalten werden.

Résumé—Le 8-hydroxyquinoléate d'uranium(VI) peut être précipité en solution homogène par de la 8-hydroxyquinoléine préparée par hydrolyse de 8-acétoxyquinoléine. La composition du chélate d'uranium formé n'est pas la même pour les deux procédés décrits de précipitation quantitative de l'uranium.

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EINE NEUE METHODE ZUR SPEKTROPHOTOMETRISCHEN BESTIMMUNG VON MIKROGRAMMENGEN TITAN

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Zusammenfassung—Es wurde eine sehr empfindliche und genaue Methode zur spektrophotometrischen Bestimmung von Mikrogrammengen Titan unter Verwendung des Azofarbstoffes Solochrome Black AS in methanolisch-salzsaurer Lösung ausgearbeitet. Dieser Farsbstoff bildet mit Titan einen rot-violett gefärbten Komplex, der bei 390 mμ maximale Absorption aufweist. Mittels dieser Methode lassen sich noch 0,1 ppm. Titan mit zufriedenstellender Genauigkeit bestimmen. Der störende Einfluss von Eisen(III), Kupfer(II), Zirkonium und Hafnium kann durch Zugabe von Ascorbinsäure und ÄDTA ausgeschaltet werden.

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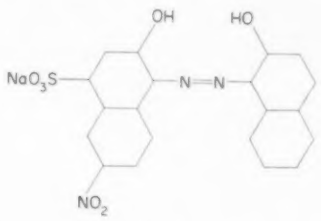
DIE vorliegenden spektrophotometrischen Untersuchungen wurden ausgeführt, um eine Methode zur photometrischen Bestimmung von Mikrogrammengen Titan zu entwickeln, die genauer und empfindlicher ist als die bis jetzt hauptsächlich verwendete Wasserstoffperoxydmethode[1] und deren Modifikationen[2,3] sowie die in unserem Laboratorium häufig benutzte Ascorbinsäuremethode.[4–8] Die hier beschriebene photometrische Methode weist eine wesentlich grössere Empfindlichkeit, als die oben genannten Verfahren auf, sodass sich Titan bei Anwendung des Azofarbstoffes Solochrome Black AS selbst in Konzentrationen unter 1 ppm. sehr genau und einfach bestimmen lässt. Die Bildung des Titan-Farbstoffkomplexes erfolgt allerdings nur in Anwesenheit organischer Lösungsmittel wie z.B. Methanol, in wässriger Lösung dagegen tritt keine Komplexbildung auf. Da die Bestimmung in relativ stark saurer Lösung durchführbar ist, wird sie durch gegebenenfalls anwesende Fremdionen praktisch nicht gestört. Die Elemente Eisen(III), Kupfer(II), Zirkonium, Hafnium, Molybdän und Vanadium sowie Phosphationen rufen die grössten Störungen hervor. Durch Zugabe von Ascorbinsäure lassen sich Eisen(III) und Kupfer(II) reduzieren bezw. maskieren, wodurch ihr Einfluss auf die Titanbestimmung ausgeschaltet werden kann. Ebenso lässt sich die durch geringe Mengen an Zirkonium bezw. Hafnium hervorgerufene Störung durch Zusatz von ADTA eliminieren. Molybdän, Vanadium und Phosphationen allerdings müssen abgetrennt werden, und zwar mittels früher entwickelter Ionenaustauschverfahren.[5–8]

EXPERIMENTELLER TEIL

Lösungen und Reagentien

(*a*) *Titanstandardlösungen.* Einer 1 n schwefelsauren Titansulfatlösung, die einen auf photometrischem Wege[1,5] ermittelten Gehalt von 1 mg Titan/ml aufwies, wurden 100 ml entnommen und in einer Platinschale weitgehendst auf dem Wasserbade eingedampft. Hierauf wurde die Schwefelsäure vorsichtig abgeraucht und das so erhaltene Titansulfat durch kurzzeitiges Glühen in Titandioxyd umgewandelt. Dieses wurde dann durch zweimaliges Abdampfen mit konz. Flussäure quantitativ in das Titanfluorid übergeführt und in insgesamt 100 ml 1 n Salzsäure aufgenommen. 1 ml dieser Lösung entsprechen 1 mg Titan. Durch entsprechendes Verdünnen mit 1 n Salzsäure wurden weitere Titanlösungen geringeren Titangehaltes hergestellt.

(*b*) *Farbstofflösung:* Da der Azofarbstoff Solochrome Black AS (Imperial Chemical Industries Ltd. Hexagon House, Blackley, Manchester, England) der Formel:



mit in Methanol unlöslichen Substanzen verunreinigt war, musste er vor seiner Verwendung folgendermassen gereinigt werden: 10–20 g des Farbstoffes wurden mit 250 ml Methanol versetzt und die Lösung einige Stunden lang unter zeitweiligem Umschütteln digeriert. Hernach wurde vom ungelösten Anteil abfiltriert und das Filtrat bei einer Temperatur von 40–50°C eingedampft. Der so erhaltene, gereinigte Farbstoff war nun rückstandslos in Methanol löslich. Für alle weiteren Versuche wurde eine 0,1%-ige methanolische Lösung des gereinigten Farbstoffes verwendet.

(*c*) *Aluminiumchloridlösung:* Eine geeignete Menge an AlCl3.6H20 p.a. wurde in 1 n Salzsäure gelöst, sodass eine Lösung entstand, die 0,4 g dieser Verbindung/ml. d.h., 44,7 mg Aluminium/ml enthielt. Sie dient zur Maskierung von Fluoridionen.

(*d*) *Lösungen anderer Elemente:* Es wurden 1 n salzsaure Lösungen vieler Kationen und Anionen hergestellt aus p.a. Reagentien verwendet.

(*e*) Ferner wurden verwendet: Chemisch reines *Methanol*, *Ascorbinsäure* (Wiener Heilmittelwerke) und eine 0,1 m *ÄDTA Lösung* (Dinatriumsalz der Äthylendiaminotetraessigsäure).

Apparatur: Die photometrischen Messungen wurden mit einem Beckman Spektrophotometer, Modell B, unter Verwendung von 1 cm-Küvetten und einer blauempfindlichen Photozelle durchgeführt.

1. *Auswahl der geeigneten Wellenlänge*

Aus einer Reihe von Messungen, die im Wellenlängenbereich von 350 bis 1000 mμ ausgeführt wurden, ging hervor, dass das Extinktionsmaximum des Titanfarbstoffkomplexes bei 390 mμ lag. Als Leerlösung wurde eine Reagensblindlösung verwendet. Alle weiteren Messungen wurden daher immer bei dieser Wellenlänge der maximalen Extinktion ausgeführt.

Die Wellenlängen maximaler Extinktion der Zirkonium-, Molybdän- und Vanadiumkomplexe des Farbstoffes liegen bei 600 mμ, 610 mμ bezw. 620 mμ. Daraus geht hervor, dass oben genannte Elemente unbedingt vom Titan abgetrennt werden müssen, wenn dieses störungsfrei bestimmt werden soll.

2. *Einfluss der Acidität*

Es zeigte sich, dass die Acidität von nur geringem Einfluss auf die Messungsergebnisse ist. Dabei ist es gleichgültig, ob die titanhaltige Lösung insgesamt 2 ml 1 n oder 3 ml 1 n Salzsäure bezw. 2 n Salzsäure pro 10 ml Messlösung enthält. Bei Anwendung höherer Salzsäurenormalitäten nimmt die Extinktion nur in geringem Masse ab. Eine Pufferung mittels Natriumacetat bringt keine Vorteile mit sich.

3. *Einfluss der Farbstoffkonzentration*

Aus einer Reihe von Versuchen ging hervor, dass sich bei Anwesenheit von 4–6 ml Farbstofflösung/10 ml Messlösung die Extinktion nicht mehr ändert, d.h., ein Konstanzbereich auftritt. Bei allen weiteren Versuchen wurden daher immer 5 ml der Farbstofflösung verwendet.

4. *Einfluss der Methanolkonzentration*

Eine Reihe bei verschiedenen Methanolkonzentrationen ausgeführte Versuche zeigten, dass die maximale Extinktion dann erreicht wird, wenn 7–8 ml Methanol/10 ml Messlösung anwesend sind. Ist die Methanolkonzentration geringer so nimmt die Extinktion bis zu einer Gesamtmethanolkonzentration von 6 ml/10 ml Messlösung ab. Unter 6 ml Methanol tritt bereits eine Ausfällung des Farbstoffes

ein, sodass Messungen in diesem Bereich unmöglich sind. Es ist daher nötig, dass die Messungen bei einer möglichst hohen Methanolkonzentration ausgeführt werden.

5. *Einfluss anderer Lösungsmittel*

Werden anstelle von Methanol andere Lösungsmittel wie z.B. Äthanol, n-Propanol, Äthylenglykol, Dioxan oder Aceton verwendet, so zeigt sich, dass keines dieser Lösungsmittel geeignet ist, da einerseits die Löslichkeit des Farbstoffes in diesen Lösungsmitteln äusserst gering ist und andererseits, wie im Falle der Anwendung von Äthylenglykol wesentlich geringere Extinktionswerte erhalten werden.

6. *Einfluss von Fremdionen*

Folgende Fremdionen stören die Titanbestimmung nicht: Al, Ni, Cr(III), Sn(II), Co, Ca, Pb, Bi(III), Zn, U(VI), U(IV), Th, Sr, Mn(II), Cd, Mg, Cl^-, $SO4^-$, $NO3^-$ und F^-.

Störungen werden durch folgende Ionen hervorgerufen: Fe(III), Cu(II), Zr, Hf, Mo und V, sowie Phosphationen.

Der störende Einfluss von selbst Milligrammengen Cu(II) und Fe(III) kann durch Zusatz von einigen Kristallen Ascorbinsäure völlig ausgeschaltet werden. Geringe Mengen an Zirkonium bezw. Hafnium lassen sich durch Zugabe von ÄDTA vollständig maskieren ohne dass dabei Titan maskiert wird. Die durch die anderen störenden Elemente hervorgerufenen Störungen können weder durch Zugabe von Ascorbinsäure noch von ÄDTA ausgeschaltet werden, Bei Anwesenheit dieser Elemente ist es daher unbedingt notig, das Titan von diesen Elementen abzutrennen. Zu diesem Zwecke wird die schon früher beschriebene Trennung des Titans als Fluoridkomplex unter Verwendung des stark basischen Anionenaustauschers Dowex 1 bezw. Amberlite IRA 400 empfohlen.[6-8] Da nach Durchführung einer derartigen Trennungsoperation das Titan als praktisch vollkommen reines Titanfluorid anfällt ist mit einer Störung der hier beschriebenen Methode nicht mehr zu rechnen. Bei der Untersuchung des Einflusses von Fremdionen wurden die einzelnen Ionen immer in 50 bis 100-fachen Überschuss gegenüber Titan angewendet. In manchen Fällen, d.h., bei Anwendung von Anionen (als Alkalisalze) wurde das betreffende Ion sogar in 1000 bis 10.000-fachen Überschuss verwendet. Bei allen Messungen war immer 1 ml der Aluminiumchloridlösung/10 ml Messlösung anwesend und zwar zur Maskierung der anwesenden Fluoridionen (siehe Herstellung der Titanlösungen). Von den störenden Ionen geben Kupfer(II) und Zirkonium bezw. Hafnium mit dem Farbstoff violett-gefärbte Komplexe. Vanadium einen graublauen, Molybdän einen blauen und Eisen(III) einen braunen Komplex.

7. *Einfluss der Zeit, Temperatur und Reihenfolge der Reagentienzugabe*

Die Komplexbildung erreicht nach 5 bis 10 Minuten ihre volle Intensität und bleibt bei einer Temperatur im Bereich von 15–30°C mehr als 5 Stunden lang konstant. Die Reihenfolge der Reagentienzugabe hat keinen Einfluss auf die Messergebnisse.

8. *Gültigkeit des Lambert Beer'schen Gesetzes*

Die zu messenden Lösungen enthielten: 0–100 μg Titan in jeweils 2 ml 1 n Salzsäure, 1 ml der Aluminiumchloridlösung, 5 ml der Farbstofflösung und den auf 10 ml fehlende Rest an Methanol. Die Extinktionen dieser Lösungen wurden dann gegenüber einer Reagensleerlösung bei einer Wellenlänge von 390 mμ gemessen. Die Ergebnisse dieser Messungen sind als Eichkurve in Abb. 1 wiedergegeben.

Wie daraus hervorgeht, wird das Lambert Beer'sche Gesetz von 1 bis 20 μg Titan/10 ml erfüllt.

9. *Empfindlichkeit und Genauigkeit der Methode*

Wie aus Abb. 1 hervorgeht, lassen sich noch 0,1 μg Titan/ml, d.i. 0,1 ppm. genau bestimmen. Der mittlere prozentuelle Fehler im Konzentrationsbereich von 1 bis 20 μg Titan beträgt $\pm 6\%$. Ist weniger als 1 μg Titan/10 ml Messlösung anwesend, so kann der Fehler bis zu $\pm 10\%$ betragen.

10 *Arbeitsvorschrift*

Die titanhaltige Lösung wird in eine geeignete Platinschale gebracht und auf dem Wasserbade zur Trockne eingedampft bezw. weitgehendst eingeengt. Gegebenenfalls anwesende Schwefelsäure muss vorsichtig abgeraucht werden. Der so erhaltene Rückstand wird zur Entfernung anwesender organischer Substanzen (wenn z.B. das Eluat nach einer Ionenaustauschoperation[6-8] eingedampft wurde)

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kurze Zeit geglüht und das so gebildete Titandioxyd durch zweimaliges Eindampfen auf dem Wasserbade mit überschüssiger konz. Flussäure in das leicht lösliche Titanfluorid übergeführt. Dieses wird dann portionsweise mit insgesamt 2 ml 1 n Salzsäure in einen 10 ml Messkolben gebracht. Die Schale wird hierauf mit 1 ml der Aluminiumchloridlösung und 1 ml Methanol ausgespült, wobei diese Waschlösungen ebenfalls in den 10-ml-Messkolben gebracht werden. Dieser Lösung werden dann 0,1 ml der ÄDTA Lösung und einige Kristalle Ascorbinsäure zur Reduktion und Maskierung von

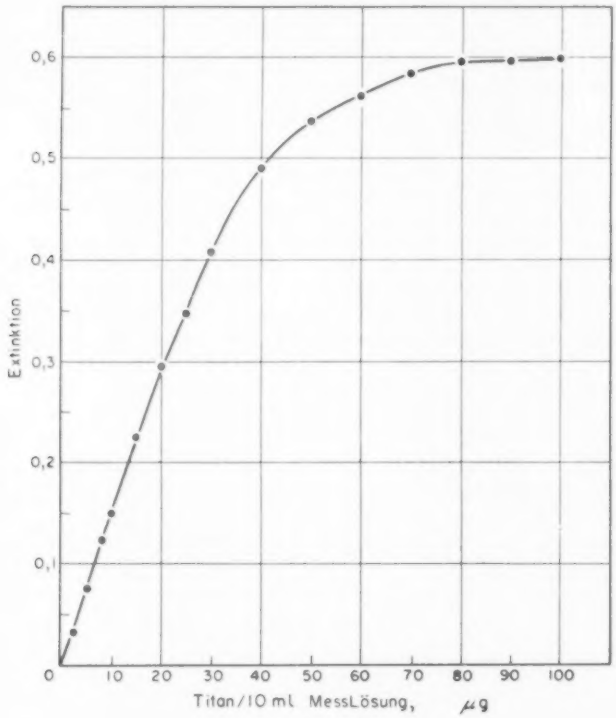

ABB. 1.

gegebenenfalls anwesenden Eisen-, Kupfer-, Hafnium- und Zirkoniumionen zugesetzt. Nach Zusatz von 5 ml der Farbstofflösung wird dann mit Methanol zur Marke aufgefüllt. Nach gründlichem Durchmischen wird dann nach Ablauf von 5–10 Minuten die Extinktion gegenüber einer Reagensleerlösung bei 390 mμ gemessen und aus der Eichkurve (Abb. 1) der Titangehalt der Messlösung ermittelt.

Summary—A very sensitive and accurate method for the spectrophotometric determination of microgram quantities of titanium has been developed. Solochrome Black AS in a hydrochloric acid-methanol medium is used as the reagent. This dyestuff reacts with titanium forming a red-violet colored complex, which shows maximum absorption at 390 mμ. By means of this method as little as 0·1 ppm. of titanium can be determined with satisfactory accuracy. The interferences of iron^{III}, copper^{II}, zirconium, and hafnium can be eliminated by the addition of ascorbic acid and EDTA.

Résumé—L'auteur a mis au point une méthode précise et très sensible pour le dosage spectrophotométrique de microgrammes de titane, en utilisant comme réactif le noir solochrome AS en milieu acide chlorhydrique. Ce colorant réagit avec le titane pour former un complexe rouge-violet qui a un maximum d'absorption à 390 mμ. Par cette méthode on peut doser 0,1 p.p.m. de titane avec une précision satisfaisante. Les interférences du fer(III), du cuivre(II), du zirconium et du hafnium peuvent être éliminées par addition d'acide ascorbique et d'EDTA.

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GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF BISMUTH USING AMMONIUM SALTS OF BENZENE AND NAPHTHALENE SELENONIC ACIDS*

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Summary—Two new reagents, $C_6H_5SeO_2NH_4$ and $C_{10}H_7SeO_2NH_4$, are suggested for the gravimetric determination of bismuth. With bismuth the reagents form white crystalline precipitates, $Bi(C_6H_{50}SeO_2)_3$ and $Bi(C_{10}H_7SeO_2)_3$, in mineral acid solutions. The bismuth is determined by weighing the precipitates after drying at 110–120°. The titrimetric determination of bismuth is possible by solution of $Bi(C_6H_5SeO_2)_3$ in a mixture of mineral and tartaric acids and iodometric titration of $C_6H_5SeO_2H$ by a potentiometric or amperometric method. The relative error of the determination of 5 to 20 mg of bismuth does not exceed 0·5%.

FOR the gravimetric determination of bismuth a number of inorganic and organic precipitants are used. One of the best methods is based on the precipitation of bismuth by selenious acid.[1–5] The determination of bismuth can be carried out as $Bi_2(SeO_3)_3$ after drying the precipitate at a temperature of 110–120°, or by a titrimetric method. The use of orthophosphoric acid and alkali metal phosphates has also been recommended.[6–8]

Arsenic acid and alkali metal arsenates form compounds with bismuth which have a very low solubility in water, similar to the phosphates.[9,10] The methods for the gravimetric and titrimetric determination and separation of bismuth as the arsenate have been little studied and have little practical significance, giving place to the use of phosphate and other methods.[11,12] Of the organic reagents for bismuth determination phenylarsonic acid, cupferron, 8-hydroxyquinoline, gallic acid, pyrogallol, *etc.*, are used.[1]

We propose two new reagents for the determination of bismuth, ammonium benzene selenonate, $C_6H_5SeO_2NH_4$, and ammonium naphthalene selenonate, $C_{10}H_7SeO_2NH_4$, which permit its determination in the presence of many other elements: Ag, Be, Ca, Al, Zn, Mn, Ni, Co, Cd, Cu, Pb, *etc.*[13]

These reagents precipitate bismuth from mineral acid solutions as crystalline precipitates, soluble in concentrated acids and decomposed by alkalies. The limiting dilution for the benzene selenonate is 1:400,000 and for the naphthalene selenonate 1:650,000. The chemical constitution of the precipitates dried at 110°, corresponds to the formula $Bi(R—SeO_2)_3$, where R is C_6H_5 or $C_{10}H_7$. The bismuth can be determined by weighing as $Bi(R—SeO_2)_3$, after drying at 110°–120°, or iodometrically.

For investigating the effect of the concentration of nitric acid on the completeness of precipitation of bismuth as $Bi(R—SeO_2)_3$, various amounts of the mineral acid were added to a nitric acid-bismuth solution. This was then diluted to 100 ml and heated to 70°–80°, and the bismuth was precipitated with $C_6H_5SeO_2NH_4$ or $C_{10}H_7$.

* Translated from the Russian, *Zhur. analit. Khim.*, 1959, **14**, 710.

SeO_2NH_4. The precipitate was washed, heated and weighed as Bi_2O_3. The results obtained are given in Fig. 1.

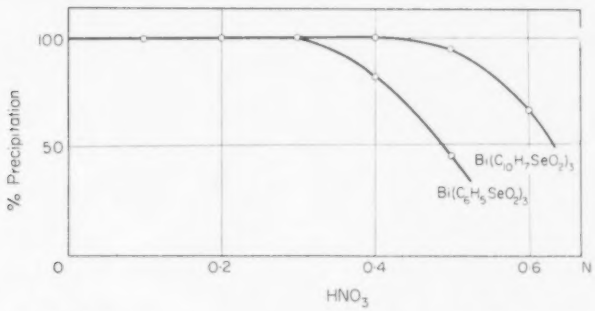
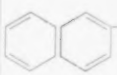


FIG. 1.—Effect of nitric acid on completeness of precipitation of bismuth as the benzene or naphthalene selenonate at reagent concentrations of 2·3%.

For the gravimetric determination of bismuth, the solution and precipitate were heated for 25–30 min on an electric hot-plate, and, after cooling, filtered through a No. 4 sintered-glass crucible. The precipitate was washed carefully with distilled water, dried at 110°–120° and weighed as $Bi(R—SeO_2)_3$.

TABLE I. DETERMINATION OF BISMUTH AS BENZENE OR NAPHTHALENE SELENINATE

Reagent	Bi taken, *mg*	Bi found, *mg*	Error, *mg*	Reagent	Bi taken, *mg*	Bi found, *mg*	Error, *mg*
SeO_2NH_4	11·26	11·25	−0·01	 SeO_2NH_4	11·26	11·27	+0·01
	11·26	11·27	+0·01		11·26	11·25	−0·01
	5·63	5·63	±0·00		5·63	5·62	−0·01
	5·63	5·61	−0·02		5·63	5·63	±0·00

The results are shown in Table I for the titrimetric determination, the benzene selenonate precipitate being dissolved in hydrochloric acid and the benzene selenonyl acid titrated iodometrically, potentiometrically or amperometrically, using a rotating platinum electrode. The residue, after precipitation of the bismuth by the benzene selenonic acid was filtered off, carefully washed with distilled water, washed into a titration flask, and a little hydrochloric acid added. Then 0·5–1·0 g of tartaric acid were added and the solution heated to complete solution of the precipitate. The solution was diluted with water, a two-three fold excess of potassium iodide added and the liberated iodine was titrated potentiometrically or amperometrically with sodium thiosulphate:

$$2C_6H_5SeO_2H + 6KI + 6HCl \rightarrow (C_6H_5Se)_2 + 3I_2 + 6KCl + 4H_2O$$

$$Bi \equiv 9I \equiv 9Na_2S_2O_3. \qquad (1)$$

At the same time, for comparison, bismuth was precipitated using selenious acid, as described in the literature.[2] The precipitate was washed with water, dissolved in

TABLE II. POTENTIOMETRIC DETERMINATION OF BISMUTH

Compound	Bi taken, *mg*	0·025*N* $Na_2S_2O_3$, *ml*	Bi found, *mg*	Error, *mg*	Compound	Bi taken, *mg*	0·025*N* $Na_2S_2O_3$, *ml*	Bi found, *mg*	Error, *mg*
$Bi_2(SeO_3)_3$	8·45	9·68	8·49	+0·04	$Bi(C_6H_5SeO_2)_3$	16·90	28·95	16·92	+0·02
	8·45	9·60	8·42	−0·03		16·90	28·97	16·93	+0·03
	4·23	4·89	4·28	+0·05		8·45	14·45	8·44	−0·01
	4·23	4·74	4·20	−0·03		8·45	14·45	8·45	±0·00
						4·23	7·23	4·23	+0·00
						4·23	7·24	4·24	+0·01

TABLE III. AMPEROMETRIC DETERMINATION OF BISMUTH

Compound	Bi taken, *mg*	0·025*N* $Na_2S_2O_3$, *ml*	Bi found, *mg*	Error, *mg*	Compound	Bi taken, *mg*	0·025*N* $Na_2S_2O_3$, *ml*	Bi found, *mg*	Error, *mg*
$Bi_2(SeO_3)_3$	4·23	4·85	4·26	+0·03	$Bi(C_6H_5SeO_2)_3$	4·23	7·23	4·23	+0·00
	4·23	4·78	4·20	−0·03		4·23	7·25	4·24	+0·01
	2·12	2·33	2·09	−0·03		2·12	3·59	2·10	−0·02
	2·12	2·46	2·16	+0·04		2·12	3·64	2·13	+0·01

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nitric acid, tartaric acid added and the liberated iodine titrated with sodium thiosulphate:

$$H_2SeO_3 + 4KI + 4HCl \rightarrow Se + 2I_2 + 4KCl + 4H_2O$$

$$Bi \equiv 6I \equiv 6Na_2S_2O_3. \quad (2)$$

The results are given in Tables II and III. It should be noted that the potentiometric and amperometric bismuth determinations using selenious acid have definite disadvantages.

The reduction of the selenious acid with potassium iodide proceeds to elemental selenium. This precipitates on the platinum electrode which then ceases to react to changes in potential. This hinders the determination of the equivalence point. For this reason potentiometric titration, even of small amounts of selenious acid, is very difficult, while amperometric titration even of small amounts of selenious acid is almost impossible. In Tables II and III the best of many results from potentiometric and amperometric titration using selenious acid are given.

Reduction of $C_6H_5SeO_2H$ with potassium iodide proceeds to diphenyldiselenide which does not affect the accuracy of determination of the equivalence point during potentiometric or amperometric titration.

Lead, at a pH not lower than 4, precipitates with the ammonium salts of benzene or napthalene selenonic acids but the large crystalline precipitate formed is very easily soluble in dilute nitric acid. On the other hand, bismuth is precipitated quantitatively by the reagents mentioned from quite acid solutions. For this reason we studied the possibility of quantitative determination of bismuth in the presence of lead. In the filtrate, after separation of the bismuth, the lead concentration was determined by precipitation with thiourea and subsequent conversion of the lead to lead chromate. The determination of the lead was carried out iodometrically.[14]

TABLE IV. DETERMINATION OF BISMUTH IN THE PRESENCE OF LEAD

Reagent	Taken, *mg*		Found, *mg*		Error, *mg*	
	Bi	Pb	Bi	Pb	Bi	Pb
	16·90	25·11	16·89	25·05	−0·01	−0·06
	16·90	25·11	16·92	—	+0·02	—
	8·45	75·33	8·48	75·35	+0·03	+0·02
	8·45	75·33	8·43	75·25	−0·02	−0·08
	5·63	150·66*	5·61	—	−0·02	—
	5·63	150·66*	5·64	150·60	+0·01	−0·06
	16·90	25·11	16·88	—	−0·02	—
	16·90	25·11	16·89	—	−0·01	—
	8·45	75·33	8·43	75·37	−0·02	+0·04
	8·45	75·33	8·48	75·24	+0·03	−0·09
	5·63	150·66*	5·65	—	+0·02	—
	5·63	150·66*	5·60	150·58	−0·03	−0·08

* Bi determined using reprecipitation.

As can be seen from the results in Table IV, if the lead content is not more than 10% of the bismuth then it does not affect the accuracy of the bismuth determination when using benzene or naphthalene selenonate. With higher concentrations of lead, the bismuth must be determined by reprecipitation.

Zusammenfassung—Zwei neue Reagenzien, $C_6H_7SeO_2NH_4$ und $C_{10}H_7SeO_2NH_4$, werden zur gravimetrischen Bestimmung von Wismuth vorgeschlagen. Beide geben mit Wismuth aus mineralsaurer Lösung weisse, kristalline Niederschläge der Zusammensetzung Bi: Reagens = 1:3. Die Niederschläge werden nach Trocknen bei 110–120°C gewogen. Die Möglichkeit wird gezeigt, Wismuth jodometrisch zu titrieren, nachdem der Niederschlag aufgelöst wird (Mischung von Mineralsäure und Weinsäure). Der Endpunkt wird amperometrisch oder potentiometrisch angezeigt. Der relative Fehler bei Bestimmungen von 5–20 mg Bi übersteigt nicht 0·5%.

Résumé—Deux nouveaux réactifs sont proposés pour le dosage gravimétrique du bismuth: $C_6H_7SeO_2NH_4$ et $C_{10}H_7SeO_2NH_4$. Les réactifs forment avec le bismuth des précipités cristallins blancs en solution d'acide minéral: $Bi(C_6H_5SeO_2)_3$ et $Bi(C_{10}H_7SeO_2)_3$. Le bismuth est pesé après séchage du précipité à 110°–120°. Les auteurs montrent qu'il est possible de faire une titrimétrie du bismuth par une solution de $Bi(C_6H_5SeO_2)_3$ dans un mélange d'acide minéral et d'acide tartrique et un titrage iodométrique de $C_6H_5SeO_2H$ par des méthodes potentiométriques ou ampérométriques. L'erreur relative du dosage de 5–20 mg. de bismuth n'excède pas 0,5 pour cent.

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USE OF TAGGED ATOMS FOR THE INVESTIGATION OF PRECIPITATE-EXCHANGE REACTIONS

PRECIPITATE-EXCHANGE WITH SILVER OXALATE

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Summary—Radiochemical investigations of precipitate-exchange reactions are suitable for the experimental determination of the equilibrium ion concentrations in these processes. This permits the separation of resultant errors determined titrimetrically into a positive and a negative error, which result respectively from the physical solubility of the exchanger precipitate, and the solubility equilibrium between the two precipitates. The authors have investigated the exchange of chloride with silver oxalate using chloride solutions containing ^{36}Cl and silver oxalate precipitates containing ^{110}Ag. The transformation ratios, determined experimentally and calculated theoretically, showed a fairly good agreement.

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PROCESSES called precipitate-exchange reactions by Ballczo and Mondl[1] are based on irreversible ion-exchanges. The dynamic solubility equilibrium between a slightly soluble precipitate (exchanger precipitate) and its saturated solution can be upset by the addition of such an ion, which forms with one of the ions of the saturated solution a precipitate of less solubility than the original one.

The equation of the process is:

$$LM\downarrow + N^- \rightleftharpoons LN\downarrow + M^-$$

In the equation LM is the exchanger, and LN represents the less soluble precipitate which is formed. The negative sign indicates the charges of the ions, but without regard to their valences.

Precipitate-exchange reactions make possible many analytical determinations.[2–8]

The equilibrium state of precipitate-exchange reactions, *i.e.* the measure of the precipitate-exchange, can be measured by the transformation ratio η. Its percentage value can be expressed by the ratio of the final concentration of the ion liberated from the precipitate, $[M^-]_r$, and the initial concentration of the newly introduced, precipitate-forming ion, $[N^-]_k$:

$$\eta\% = \frac{Y[M^-]_v}{Z[N^-]_k} 100 . \qquad (1)$$

In equation (1), Y and Z represent the valences of the corresponding ions.

The initial and final concentrations can be calculated using the following equations:

$$Y[M^-]_v = Y\{[M^-]_r + [M^-]_o\} \qquad (2)$$

$$Y[M^-]_r = Z\{[N^-]_k - [N^-]_v\} \qquad (3)$$

$$Z[N^-]_k = Y\{[M^-]_v - [M^-]_o\} + Z[N^-]_v . \qquad (4)$$

In these equations, $[M^-]_r$ represents the concentration of M^- ions formed during the precipitate-exchange process, and $[M^-]_o$ means the concentration of the exchanger precipitate arising from physical dissolution. $[N^-]_v$ represents the untransformed part of the precipitate-forming ion concentration. Values of $[M^-]_o$ and $[N^-]_v$ can be calculated, using the law of mass action, from the solubility products of the corresponding precipitates. If the value of $[N^-]_k$ is known from the original weighing, and that of $[M^-]_v$ is determined by titration, the transformation ratio of single precipitate-exchange reactions can be determined experimentally.

Measurements in the case of some reactions, carried out with various $[N^-]_k$ values,[9–12] have shown that the transformation ratios are usually less than 100%; that is, these reactions are not completely stoichiometric in all concentration ranges. The experimental control of precipitate-exchange reactions registers only this fact, but gives no further information about the real processes occurring in precipitate-exchanges, because the $[M^-]_o$ and $[N^-]_v$ values cannot be determined by titrations. Their experimental determination is, however, possible by means of "tagged" atoms.

In this paper, the experimental investigation of chloride-exchange with silver oxalate is described, and the results are compared with those calculated from the solubility products.

THEORETICAL

The precipitate-exchange reaction mentioned by Sendroy,[5]

$$Ag_2C_2O_4 \downarrow + 2Cl^- \rightleftharpoons 2AgCl \downarrow + C_2O_4^{--},$$

can be used for the quantitative determination of chloride ion.

The equilibrium ion concentrations, characteristic for the exchange reaction, can be calculated from the solubility products of the $Ag_2C_2O_4$ and AgCl precipitates. Since the initial chloride ion concentration, $[Cl^-]_k$, was known, the values of $[Cl^-]_v$, $[C_2O_4^{--}]_o$, $[C_2O_4^{--}]_r$ and $[C_2O_4^{--}]_v$ were calculated, as follows:

$$L_{AgCl} = [Ag^+][Cl^-]_v , \tag{5}$$

and

$$L_{Ag_2C_2O_4} = [Ag^+]^2[C_2O_4^{--}]_r . \tag{6}$$

From equations (5) and (6),

$$[Cl^-]_v = \frac{L_{AgCl}}{[Ag^+]} ; \qquad [Ag^+] = \sqrt{\frac{L_{Ag_2C_2O_4}}{[C_2O_4^{--}]_r}} .$$

Thus

$$[Cl^-]_v = \frac{L_{AgCl}}{\sqrt{\frac{L_{Ag_2C_2O_4}}{[C_2O_4^{--}]_r}}} .$$

From equation (3),

$$2[C_2O_4^{--}]_r = [Cl^-]_k - [Cl^-]_v ,$$

and, after substitution, squaring and multiplying we obtain the relation,

$$[Cl^-]_v^2 = \frac{L_{AgCl}^2 [Cl^-]_k}{2 L_{Ag_2C_2O_4}} - \frac{L_{AgCl}^2 [Cl^-]_v}{2 L_{A_2C_2gO_4}} ,$$

which yields the quadratic equation,

$$2L_{Ag_2C_2O_4}[Cl^-]_v^2 + L_{AgCl}^2[Cl^-]_v - L_{AgCl}^2[Cl^-]_k = O \qquad (7)$$

In calculating $[Cl^-]_v$ values from equation (7) only the positive root of the quadratic equation was taken into consideration. This method of calculation, however, can only be used if the requirement

$$[C_2O_4^{--}]_o \ll [C_2O_4^{--}]_r$$

is fulfilled. In this case

$$[C_2O_4^{--}] = \frac{[Ag^+]}{2},$$

and using equations (6) and (3),

$$[C_2O_4^{--}]_o = \sqrt{\frac{L_{Ag_2C_2O_4}}{2\{[Cl^-]_k - [Cl^-]_v\}}}.$$

The value of $[C_2O_4^{--}]_v$ can be calculated using equations (4) and (3).

$$[C_2O_4^{--}]_v = \frac{[Cl^-]_k - [Cl^-]_v}{2} + [C_2O_4^{--}]_o$$

$$= [C_2O_4^{--}]_r + [C_2O_4^{--}]_o$$

The percentage value of the transformation ratio is then given by

$$\eta\% = \frac{[C_2O_4^{--}]_v}{[Cl^-]_k} \cdot 100 .$$

Chloride exchange with silver oxalate was examined only in neutral medium. In acidic medium, the solubility of silver oxalate increases considerably. In an aqueous solution of silver oxalate the following equilibrium exists:

$$Ag_2C_2O_4\downarrow \rightleftharpoons 2Ag^+ + C_2O_4^{2-} . \qquad (I)$$

In the presence of hydrogen ions there is the further equilibrium,

$$2H^+ + C_2O_4^{2-} \rightleftharpoons (COOH)_2 . \qquad (II)$$

In acidic medium, therefore, oxalate anions form with protons poorly dissociating oxalic acid molecules. Because of this, the oxalate ion concentration decreases, and therefore, according to equation (I), further amounts of silver oxalate must dissolve in order to re-establish the solubility equilibrium. It has also been proven experimentally that chloride-exchange with silver oxalate cannot be carried out in sulphuric acid solutions more concentrated than 0.01*N*.[10]

In alkaline medium the solubility of silver oxalate also increases. In the presence of alkali hydroxides, silver oxide is formed according to the following reaction:

$$2Ag^+ + 2OH^- \rightleftharpoons Ag_2O\downarrow + H_2O.$$

In ammoniacal solutions the silver-ammine complex is formed:

$$2Ag^+ + 4NH_3 \rightleftharpoons 2[Ag/NH_3/_2]^+.$$

Both processes decrease the concentration of silver ions in the saturated solution of

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silver oxalate, that is, they increase the solubility of silver oxalate. Chloride-exchange in alkaline media therefore cannot be used with silver oxalate.

Values of the equilibrium ion concentrations, calculated from the equations quoted, are given in Table I. For the solubility product of silver oxalate the value $1{\cdot}3 \times 10^{-11}$ (at 25°) was obtained from the literature.[13]

TABLE I.—CALCULATED VALUES OF EQUILIBRIUM ION CONCENTRATIONS (NEUTRAL MEDIUM)

$[Cl^-]_k$, *mmole/litre*	$[Cl^-]_v$, *mmole/litre*	Negative error, %	$[C_2O_4^{--}]_o$, *mmole/litre*	$[C_2O_4^{--}]_r$, *mmole/litre*	positive error, %	$[C_2O_4^{--}]_v$, *mmole/litre*	η, %
50·000	0·018	0·04	0·011	24·991	0·04	25·002	100·01
40·000	0·017	0·04	0·013	19·992	0·07	20·005	100·02
20·000	0·012	0·06	0·018	9·994	0·18	10·012	100·16
10·000	0·009	0·09	0·026	4·996	0·52	5·022	100·44
4·000	0·005	0·14	0·040	1·997	2·00	2·001	101·87
2·000	0·003	0·19	0·057	0·998	5·71	1·055	105·52
1·000	0·002	0·27	0·081	0·499	16·24	0·580	115·97

$t = 25°$: $L_{AgCl} = 1{\cdot}6 \times 10^{-10}$; $L_{Ag_2C_2O_4} = 1{\cdot}3 \times 10^{-11}$

EXPERIMENTAL

Precipitate-exchange carried out with NaCl* and $Ag_2{}^*C_2O_4$ enables the experimental determinations of $[Cl^-]_v$ and $[C_2O_4^{--}]_o$ values to be made; that is, the determination of the amounts of chloride ions which took no part in the exchange reaction, as well as the physical solubility of the exchanger precipitate. Thus, using equations (2) and (3), values of $[C_2O_4^{--}]_r$ and $[C_2O_4^{--}]_v$ can also be calculated.

The NaCl* solution used for our experiments, contained a β-radiating ^{36}Cl isotope ($t_{1/2} = 3{\cdot}6 \times 10^5$ years), and the $Ag_2{}^*C_2O_4$ precipitate contained a β-radiating ^{110}Ag isotope ($t_{1/2} = 270$ days).

Reagents

Inactive 0·1*N* NaCl solution, active NaCl* solution of 0·1 μC/ml specific activity, as well as inactive and active silver oxalate precipitates (the latter of known specific activity) were used.

Preparation of silver oxalate suspensions: The inactive silver oxalate was prepared by precipitation from silver nitrate solution with a small excess of oxalic acid, using 34 g of silver nitrate dissolved in 400 ml of water and 14 g of crystallised oxalic acid ($C_2H_4O_2{\cdot}2H_2O$) dissolved in 500 ml of water. To free it from excess of the precipitant, the precipitate was washed with water 8–10 times by decantation. The silver oxalate obtained in this way had a negative surface charge, and therefore no surface adsorption of active Cl^- ions occured in the reactions with tagged NaCl solutions.

The active silver oxalate suspension was prepared in a similar way, but the precipitation was carried out in oxalic acid solution using an excess of silver nitrate. In this way, the surface of the precipitate becomes positively charged and so it does not adsorb active Ag^+ ions formed by the exchange reaction.

Experimental determination of $[Cl^-]_v$ *values*

A known amount of sodium chloride solution of a known activity was pipetted into a 50-ml volumetric flask, and was mixed with a small excess of the inactive silver oxalate suspension. In order to coagulate the silver chloride formed by the reaction, 1 ml of 20% sodium nitrate solution was added, and after diluting to the mark, the mixture was shaken thoroughly. Then the mixture was shaken in a reagent bottle for 0.5 hr using a mechanical shaker, and was then placed in a thermostat bath at 25° for 3 hr. During this time the mixture was occasionally shaken. After separation by centrifuging the specific activity of the pure solution was measured.

The specific activity of the NaCl solution used was 0·1 μ C/ml, which gave a value of 12800 i/p in our counter. Using this solution, we did not obtain measurable $[Cl^-]_v$ values for any initial chloride

concentrations; *i.e.* the values of the activities, corrected by background values, were zero. It might be assumed theoretically that by using NaCl* solution of higher specific activities, the measured $[Cl^-]_v$ values would be increased. But this assumption is not supported by the fact that the measured transformation ratios agree well with the calculated ones, using zero values for $[Cl^-]_v$, and so for the negative error of the precipitate-exchange reaction.

Determination of $[C_2O_4^{--}]_o$ *values*

Known amounts of inactive sodium chloride solutions were mixed together with a small known amount in excess, of active silver oxalate suspension, as in the above procedure. The activity of the amount of silver oxalate used—in a 50-ml final volume—was also determined. From the solubility product of silver oxalate and from the silver ion concentration determined by activity measurements, the $[C_2O_4^{--}]_o$ value could be calculated.

Activity measurements

Activities of the solutions were measured with a liquid counter, produced in the Institute of Physical Chemistry of the Technical University of Budapest (Fig. 1.). The calix-like counter-tube has a thin wall and is mounted with an aquadag-cathode, and so is suitable for β-counting.

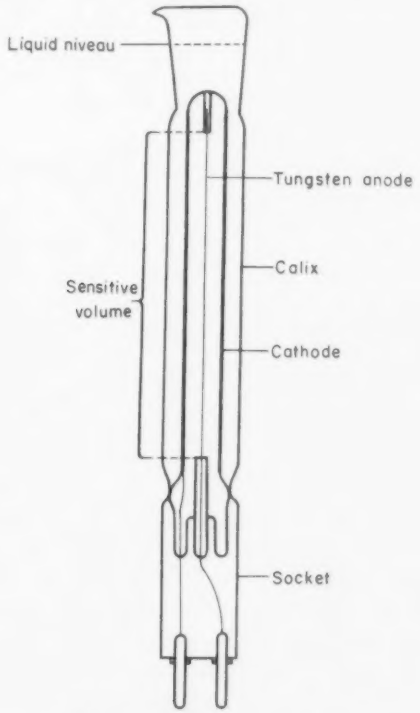

FIG. 1.—Liquid counter tube.

Instead of evaporating the solution on small aluminium plates, and counting with an end-window GM-tube, the use of the liquid scaler was preferred because of the small specific activities of most of the solutions measured.

Since the final volumes of the solutions were about 50 ml, and the counter tube had a volume of approximately 18 ml, two parallel measurements could be carried out. The tube was filled with solution so that the surface of the solution was 1 cm below the edge of the tube. In this way the volumes corresponding to the activities measured were determined by the sensitive volume of the scaler tube, and the measured activities were proportional to the specific activities of the solutions.

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Because of the small concentrations of the solutions, the error caused by self-absorption at various concentrations was negligible.

The background was measured before each activity measurement, to avoid errors from contaminants adsorbed from the preceding measurements. After four or five measurements, as the increase of background activity became considerable, the tube was washed with concentrated nitric acid, and in this way the background was kept at a sufficiently low level for each measurement. For background measurements the tube was filled with distilled water.

The counts were made with the ten-divided scaler, type EMG 1872.

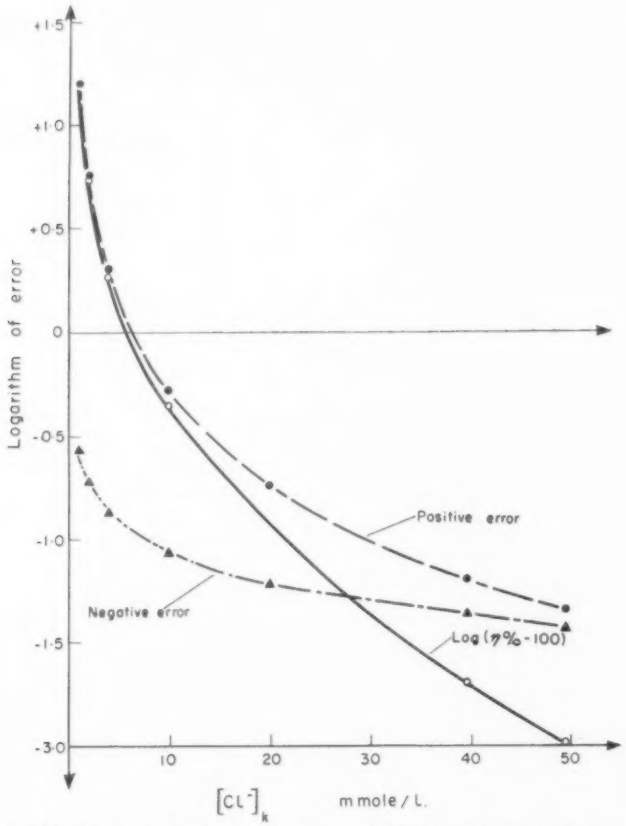

FIG. 2(*a*)—Theoretical values of the errors of chloride-exchange with silver oxalate.

RESULTS AND DISCUSSION

The experimental results for equilibrium ion concentrations obtained from activity measurements are shown in Table II. In the column "titr. $\eta\%$" is given the transformation ratio calculated from titrimetric measurement of the oxalate ion liberated during the reaction, using an iodometric method.[10]

The experimental results, in agreement with the theoretically calculated ones, show that the chloride exchange is not stoichiometric at any initial chloride concentration.

Although the calculated and measured values of the transformation ratios agree well in the range 50·00–10·00 mmole/litre initial concentration, it does not follow that

the positive and negative errors of the exchange reactions, as measured by activities, also agree with the calculated values.

TABLE II.—EXPERIMENTAL VALUES OF EQUILIBRIUM ION CONCENTRATIONS (NEUTRAL MEDIUM)

$[Cl^-]_k$, *mmole/litre*	$[Cl^-]_v$, *mmole/litre*	Negative error, %	$[C_2O_4^{--}]_o$, *mmole/litre*	$[C_2O_4^{--}]_r$, *mmole/litre*	Positive error, %	$[C_2O_4^{--}]_o$, *mmole/litre*	η, %	titr. η, %
50·000	0·0	0·0	0·006	25·000	0·024	25·006	100·02	
40·000	0·0	0·0	0·007	20·000	0·035	20·007	100·04	100·65
20·000	0·0	0·0	0·010	10·000	0·100	10·010	100·10	101·10
10·000	0·0	0·0	0·014	5·000	0·280	5·014	100·28	102·60
4·000	0·0	0·0	0·020	2·000	1·000	2·020	101·00	104·40
2·000	0·0	0·0	0·026	1·000	2·600	1·026	102·60	115·40
1·000	0·0	0·0	0·034	0·500	6·800	0·534	106·80	

$t = 25°$

The calculated value of the negative error, $\frac{[Cl^-]_v}{[Cl^-]_k} \cdot 100$, increases at 25° with the initial chloride concentration; in our experiments no negative error could be demonstrated.

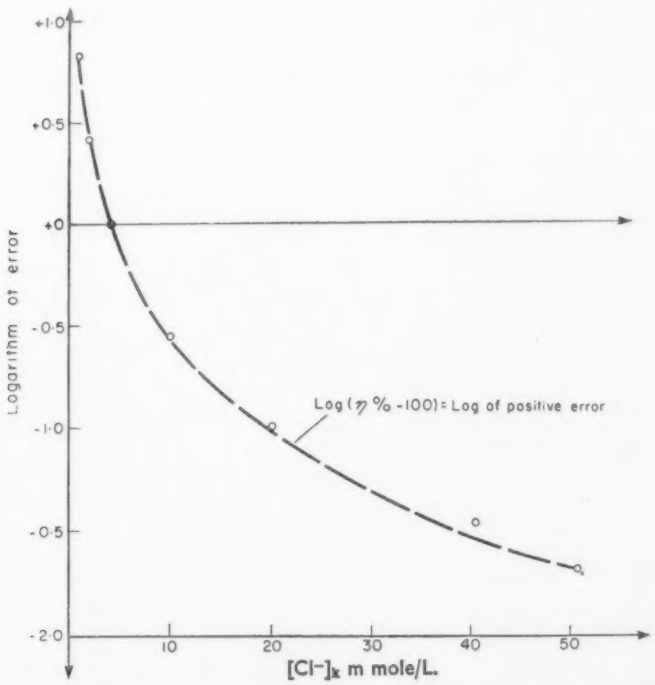

FIG. 2(*b*)—Experimental values of the errors of chloride-exchange with silver oxalate.

The positive error, $\frac{[C_2O_4^{--}]_o}{[C_2O_4^{--}]_r} \cdot 100$, determined experimentally, and arising from the physical solubility of silver oxalate, is also smaller than the theoretically calculated values above an initial concentration of 20·00 mmole/litre. For smaller initial

chloride ion concentrations, however, this error is greater than the theoretical value.

The experimental results indicate that the chloride ion-exchange with silver oxalate can be used for analytical purposes at concentrations above 10 mmole/litre.

Fig. 2(*a*) shows the theoretical, and 2(*b*) the experimental values of the errors of the reaction as a function of the initial chloride ion concentration.

The deviation of the experimental transformation ratios from the "titr. $\eta\%$" values can be explained by the fact that errors determined by activity measurements result only from the solubilities and concentrations, while in values of the transformation ratios determined titrimetrically, all the errors caused by reactions in the liquid phase, as well as the errors of the titrimetric methods, are involved.

Zusammenfassung—Radiochemische Untersuchungen sind geeignet um die Austauschreaktionen an Niederschlägen zu studieren. Fehler können in zwei Gruppen geteilt werden: positive und negative. Die Fehler rühren her, von "physikalischer Löslichkeit" der Austauschniederschläge und dem Löslichkeitsgleichgewicht der beiden Niederschläge. Der Austausch von Chlorid mit Silberoxalat wurde untersucht, wobei Lösungen verwendet wurden, die ^{36}Cl und ^{110}Ag enthielten. Die experimentell bestimmten. Austauschkoeffizienten stimmen mit den theoretisch berechneten gut überein.

Résumé—Les études radiochimiques des réactions d'échange des précipités conviennent pour la détermination expérimentale des concentrations d'ions en équilibre dans ces procédés. Par conséquent, les erreurs résultantes peuvent être divisées en une erreur positive et une erreur négative, dues à la solubilité physique du précipite échangé et à l'équilibre de solubilité entre les deux précipités. L'échange du chlorure avec l'oxalate d'argent a été étudié en utilisant des solutions contenant ^{36}Cl et ^{110}Ag. Les rapports de transformation, déterminés expérimentalement et calculés théoriquement, sont en bon accord.

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THE DETERMINATION OF TRACES OF PALLADIUM IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A method is described for the determination of traces of palladium in samples of platinum by neutron-activation analysis. In order to avoid self-shielding differences between samples and standards during neutron-irradiation, standards have been prepared by the addition of very small known amounts of palladium to analytical samples. Each determination required 0·1 g of sample, and a radiochemical procedure using carriers has been employed to isolate the induced palladium activity.

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INTRODUCTION

A NEUTRON-ACTIVATION procedure has been developed for the determination of traces of palladium in samples of platinum. The method has been evolved to provide greater sensitivity than is available with most conventional analytical procedures. Neutron-activation has been used previously to determine traces of palladium in meteorites,[1] rocks,[2] enzyme solutions,[3] and nickel.[4]

Naturally occurring palladium consists of six isotopes ^{102}Pd (% abundance, θ = 0·96), ^{104}Pd (θ = 10·97%), ^{105}Pd (θ = 22·2%), ^{106}Pd (θ = 27·3%), ^{108}Pd (θ = 26·7%) and ^{110}Pd (θ = 11·8%). On irradiation with neutrons of thermal energies the element yields radionuclides; the following sequences are the most important:

$$^{102}\text{Pd} \xrightarrow{n,\gamma} {}^{103}\text{Pd}\ (t_{\frac{1}{2}} = 17\cdot0\text{d}) \xrightarrow{EC} {}^{103}\text{Rh (stable)}$$

$$^{108}\text{Pd} \xrightarrow{n,\gamma} {}^{109m}\text{Pd}\ (t_{\frac{1}{2}} = 4\cdot75\ \text{min}) \xrightarrow{IT} {}^{109}\text{Pd}\ (t_{\frac{1}{2}} = 13\cdot5\ \text{hr}) \xrightarrow{\beta^-} {}^{109}\text{Ag (stable)}$$

$$^{110}\text{Pd} \xrightarrow{n,\gamma} {}^{111m}\text{Pd}\ (t_{\frac{1}{2}} = 5\cdot5\ \text{hr}) \xrightarrow{IT\ (75\%)} {}^{111}\text{Pd}\ (t_{\frac{1}{2}} = 22\ \text{min}) \xrightarrow{\beta^-} {}^{111}\text{Ag}\ (t_{\frac{1}{2}} = 7\cdot6\text{d}) \xrightarrow{\beta^-} {}^{111}\text{Cd(stable)}$$

$$^{110}\text{Pd} \xrightarrow{n,\gamma} {}^{111}\text{Pd}\ (t_{\frac{1}{2}} = 22\ \text{min}) \xrightarrow{\beta^-} {}^{111}\text{Ag}\ (t_{\frac{1}{2}} = 7\cdot6\text{d}) \xrightarrow{\beta^-} {}^{111}\text{Cd(stable)}$$

$$^{110}\text{Pd} \xrightarrow{n,\gamma} {}^{111m}\text{Pd}\ (t_{\frac{1}{2}} = 5\cdot5\ \text{hr}) \xrightarrow{\beta^-\ 25\%} {}^{111}\text{Ag}\ (t_{\frac{1}{2}} = 7\cdot6\text{d}) \xrightarrow{\beta^-} {}^{111}\text{Cd(stable)}$$

Relevant isotopic thermal neutron activation cross-sections, σ, are:[5]

^{102}Pd	4·8 barns
^{108}Pd	10 (13.6 hr)
^{110}Pd	0·3 (22 min).

Activity of the radionuclide 13·5-hr palladium-109 was measured in the present study. Jenkins and Smales[6] have estimated that with a thermal neutron flux of 10^{12} neutrons/cm^2/sec, as available in the Harwell Pile BEPO, *ca.* 10^{-10} g of palladium may be determined under ideal conditions using ^{109}Pd. Palladium-109 decays by the

emission of β^--particles of maximum energy 1·02 Mev, γ-rays of energies 0·307, 0·320, 0·325, 0·412, 0·425, 0·448, 0·55, 0·64 and 0·77 Mev (all weak) are also emitted.[7]

To avoid neutron self-shielding differences between samples and standards, in the present work standards have been prepared by the admixture of small known quantities of palladium with analytical samples.

EXPERIMENTAL

Irradiation

The samples for analysis were in the form of metal sponge and were ground to small fragments. Suitable quantities (*ca.* 0·1 g) were weighed and sealed in silica ampoules made from silica tubing of internal diameter 4 mm. Standards were prepared by adding weighed portions (*ca.* 0·05 g) of a standard solution of palladium (27·6 mg of Pd/litre) to 0·1-g samples of the platinum in silica ampoules. The liquid in the tubes was allowed to soak into the metal powder, and then was carefully evaporated to dryness, after which the ampoules were sealed.

Standards containing the added palladium, and samples to which no palladium had been added, were packed together with silica wool in standard aluminium cans, 3 in. × 1 in., for irradiation in BEPO. Irradiation was for periods of up to 3 days at Pile Factor 10 (thermal neutron flux 10^{12} n/cm²/sec). On delivery from Harwell after irradiation, the samples and standards were analysed radiochemically for ^{109}Pd by the procedure described below.

Radiochemical separation procedure

Carriers were employed in the isolation of the radiopalladium. An initial separation was achieved by precipitation of palladium dimethylglyoxime from dilute acid solution and additional purification was attained by precipitation of hydrous palladium dioxide. Further reduction in the contamination of the palladium was effected by precipitation and solvent extraction of the dimethylglyoxime derivative. Although gold is reported not to be precipitated by dimethylglyoxime under the conditions employed in the procedure,[8] it was necessary to remove the final traces of the element by extraction with ethyl acetate. By this stage ^{111}Pd had completely decayed away and any residual silver activity was removed by a silver chloride scavenge. The purified palladium was finally precipitated and counted as the dimethylglyoxime derivative. Experimental details are as follows:

Step 1: Transfer the irradiated samples and standards to 250-ml beakers. Wash out the irradiation ampoules with warm 6*M* HCl and add the washings to the beakers. To each sample add 1 ml of Pd carrier (7 mg of Pd/ml as $PdCl_2$ in dil HCl, standardised gravimetrically as palladium dimethylglyoxime). Add 5 ml of *aqua regia* and slowly dissolve the platinum. Dilute to 200 ml with cold water.

Step 2: Add 2 ml of a 1% solution of dimethylglyoxime in 95% ethanol and stir vigorously until the precipitated palladium complex has been coagulated. Collect the precipitate by filtration on a No. 41 Whatman paper and wash it with small portions of cold 2*M* HCl and cold water.

Step 3: Transfer the precipitate to a 250-ml beaker, and evaporate with two 3-ml portions of 16*M* HNO_3. Dilute to 100 ml with water, add 5 ml of 5% $Hg(NO_3)_2$ solution and boil. Add 5 ml of 10% $NaBrO_3$ solution and digest on a hot-plate until the blackish-brown precipitate of hydrous PdO_2 has settled. Collect the precipitate on a No. 41 Whatman paper and wash it with hot water.

Step 4: Transfer the precipitate to a 250-ml beaker, add 3 ml of 12*M* HCl, and dilute with exactly 100 ml of cold water. Add 2 ml of 1% dimethylglyoxime reagent and stir for 2 min. Add 30 ml of 12*M* HCl, stir, and transfer the suspension to a 250-ml separating funnel. Extract the palladium complex into a 50-ml and two 10-ml portions of $CHCl_3$.

Step 5: Combine the organic extracts and evaporate to dryness. Dissolve the precipitate in 1 ml of 16*M* HNO_3 containing a few drops of 12*M* HCl. Add 2 mg of Au carrier (as $AuCl_3$ in 1*M* HCl) and 5 ml of 12*M* HCl, and boil for 5 min. Dilute the solution to 100 ml with water and extract the gold with three 10-ml portions of ethyl acetate. Retain the aqueous phase in two clean 50-ml centrifuge tubes.

Step 6: To each portion of the aqueous solution add 2 mg of Ag carrier (as $AgNO_3$ in water), and centrifuge. Transfer the supernates to two clean 50-ml centrifuge tubes. To each add 2 ml of

dimethylglyoxime reagent. Centrifuge and discard the supernates. Combine together the two precipitates of palladium dimethylglyoxime and wash with small portions of water and 95% ethanol. Slurry the precipitate with 95% ethanol on to a weighed aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068), by using a transfer pipette. Make sure that the distribution of the precipitate on the tray is uniform. Dry at 110° for 15 min, cool, and weigh to establish the chemical yield.

Counting of the isolated palladium dimethylglyoxime precipitates

Final precipitates of the palladium dimethylglyoxime complex, $Pd(C_4H_7N_2O_2)_2$, prepared by the above procedure from analysis samples and standards were counted under identical conditions with a thin end-window Geiger-Müller counter. All observed counting rates were corrected for paralysis, background and chemical yield. No correction for self-absorption of β-radiation in the precipitates was necessary as they were all kept nearly the same in weight. Decay characteristics of all the precipitates were measured to ensure that the activities were due to ^{109}Pd; typical decay curves are shown in Fig. 1.

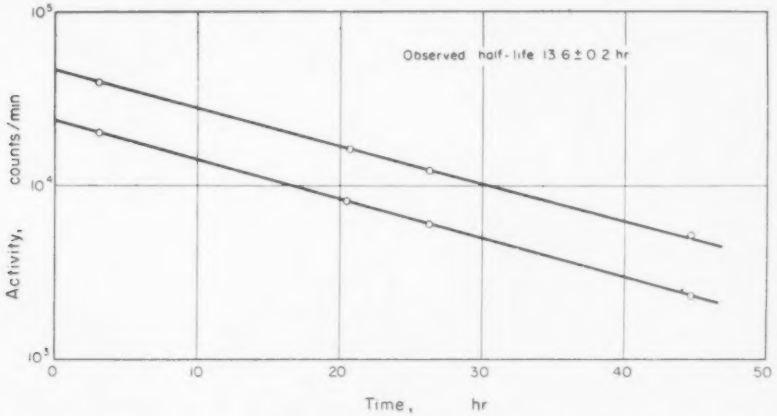

FIG. 1.—Typical decay curves.

RESULTS

In Table I are shown results of analyses of pure samples of platinum.

TABLE I. PALLADIUM CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Palladium content, *ppm*
Pt 1	0·36, 0·31
Pt 2	0·7, 0·7, 0·8, 0·8, 0·8, 0·8*
Pt 3	2·16, 2·12, 2·12, 2·13
Pt 4	0·40, 0·34
Pt 5	1·73, 1·81
Pt 6	3·17, 3·14, 2·72, 2·68
Pt 7	1·20, 1·17

* These results are quoted to only one significant figure because the measured activities were rather low because of an unavoidable delay in this run.

The major advantages of the present method over the spectrographic methods previously used in studying the contamination of platinum with palladium are the

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greatly improved sensitivity, and the avoidance of difficulties in the preparation of suitable comparison standards.

Acknowledgement—We are grateful to the Mond Nickel Co. Ltd. for the loan of samples of platinum, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zusammenfassung—Eine Methode zur Bestimmung von Palladium in Platin mittels Neutronenaktivierungsanalyse wird beschrieben. Um Unterschiede in der Selbstabeschirmung von Standard und Probe zu vermeiden, wurden Standards durch Zusatz gemessener Mengen von Palladium zu analytischen Proben hergestellt. Jede Bestimmung benötigt 0,1 g Probenmaterial. Radiochemische Verfahren unter Heranziehung von Trägern wurden angewandt um die induzierte Palladiumaktivität zu isolieren.

Résumé—Les auteurs décrivent une méthode de dosage de traces de palladium dans des échantillons de platine par analyse par activation de neutrons. Afin d'éviter des différences d'auto-protection entre les échantillons et les étalons pendant l'irradiation neutronique, les étalons ont été préparés par addition de très faibles quantités connues de palladium aux échantillons analytiques. Chaque dosage nécessite 0,1 g d'échantillon; une méthode radiochimique utilisant des entraineurs a été utilisée pour isoler l'activité induite du palladium.

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STUDIES ON URONIC ACID MATERIALS—III*

AN INVESTIGATION, USING ^{14}C COMPOUNDS, OF ACID DECARBOXYLATION REACTION-TIMES

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Summary—The reaction-times for complete (*i.e.* 99%) decarboxylation of glucuronic acid labelled at C6 with ^{14}C are respectively 200 min and 360 min, from start of reflux, for 19% and 12% (w/w) aq. hydrochloric acid. The corresponding first-order rate constants are $7{\cdot}4 \times 10^{-4}$ sec^{-1} and $1{\cdot}6 \times 10^{-4}$ sec^{-1}. Because of the simultaneous production of carbon dioxide from side reactions, however, analytically correct results are given, by compensation of errors, in shorter times, *i.e.* in 140–160 min for 19% acid and in 270–290 min for 12% acid. The results also indicate that the use of 19% acid minimises the error arising from spurious production of carbon dioxide in side reactions: this is contrary to some published opinions.

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THE quantitative analysis of uronic acid groups is of great importance in investigations of plant gums[1] and other carbohydrate materials, in the analysis of foodstuffs and of organic matter in soils, and in animal[2] and plant[3] biochemistry. The analytical problems presented by uronic acid materials offer a considerable challenge to the chemist.

Lefèvre and Tollen's classical decarboxylation method[4] was based on Mann and Tollen's earlier experiments[5] with glucuronic acid and 12% (w/w) aq. hydrochloric acid. Although the reaction was formulated as

$$\underset{\text{a hexuronic acid}}{C_6H_{10}O_7} \rightarrow \underset{\text{furfural}}{C_5H_4O_2} + CO_2 + 3H_2O$$

the yield of furfural is always much less than theoretical[6] at the reaction-time giving 1 mole of carbon dioxide. Side-reactions, which are complex,[7,8,9] therefore take place; they begin as soon as decarboxylation of a uronic acid molecule, resulting in the formation of an acid-labile decomposition product, is first achieved. Since carbon dioxide is liberated from these side-reactions slowly and approximately linearly with time, yields in excess of 1 mole must result[10] if the reflux period necessary for 100% decarboxylation is used.‡ There is no known method of eliminating these side-reactions. The analytically correct time, even for pure reference uronic acids, is therefore, by compensation of errors, less than the full time required for complete decarboxylation.

The complex system of reaction products cannot readily be reconstructed for study as a synthetic mixture; the uronic acid and its successive reaction products form a dynamic, integrated system which at present can only be studied as a whole. Consequently, it is not surprising that widely differing times for complete decarboxylation have been proposed. Thus for 12–13% hydrochloric acid the literature includes such

* Part II—see ref. 1.

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‡ Since first-order reactions are never absolutely complete, > 99% decarboxylation is here referred to as "complete" or "total" decarboxylation.

periods as 3 to 4 hr,[4,6,11] 8 hr[12,13] and 15 hr;[14] 70 min[15] and 3–4 hr[16] have been proposed for 12–13% hydrochloric acid saturated with sodium chloride. A reaction period of 4 hr was suggested[17] for *both* 13% and 18% hydrochloric acid. For 19% acid, reflux for 1·5 hr was first proposed;[18] this has been increased in more recent papers to 2 hr[19] and to 2·5 hr.[20]

A study of the analytical chemistry of uronic acids has been made over the past 5 years.[21] Comparison of the results given by the classical decarboxylation reaction with those obtained by (*a*) thermal decarboxylation[22] and (*b*) colorimetric methods (*cf.* ref. 20) indicated that the decarboxylation method was by far the most reliable. It was therefore important to verify the correct reaction-time for a given set of conditions. This was facilitated when potassium-D-glucuronate, labelled at C_6 (the carboxyl group) with ^{14}C, became available.

EXPERIMENTAL

^{14}C-*labelled compounds*

Barium carbonate-^{14}C and potassium-D-glucuronate-6-^{14}C were purchased from the Radiochemical Centre, Amersham, England. The certificated radiochemical purity of the glucuronate at the time of purchase was quoted as 101%, but this material was kept in storage for 2 yr, and its purity was only 92–93% at the time of use in these experiments. (*cf.* ref. 23).

Counting

The carbon dioxide evolved from labelled compounds was swept by the nitrogen scrubbing gas through a scintillation cell [Nuclear Enterprises (G.B.) Ltd.] mounted in a photomultiplier: the cell was designed for high efficiency counting of ^{14}C labelled vapours. The photomultiplier was attached to a probe unit (Type 1014A) whose pulse output was counted on a two-decade fast scaler (Type 1009B) fitted with a three-decade electronic register. Preliminary experiments showed, however, that absorption of carbon dioxide occurred on the plastic surfaces of the scintillation cell, giving a large residual count which persisted for several hours. The small amounts of furan, *etc.*, evolved[24] as reaction products from uronic acids may have had a slight solubilising effect on the plastic surfaces, leading to some entrainment of carbon dioxide. The scintillation cell was therefore replaced by a flow-cell of special design*; the mica end-window (1·9 mg/cm^2 window density) of a Geiger tube acted as one wall of the cell. The Geiger tube (fed from a power unit, Type 1007 with a suitable potentiometer) was not so efficient as the photomultiplier, but showed much better response to changes in the ^{14}C concentration. It was therefore used in all the experiments reported.

Preliminary experiments with labelled barium carbonate

The decarboxylation apparatus used was originally designed[20] to facilitate both analytical determinations and kinetic studies. The amount of "dead-space" had been minimised, but a potential source of error lay in the possible absorption of carbon dioxide in droplets of water adhering to the cold condenser surfaces. At the outset it appeared that this effect was unlikely to be significant, since the total volume of carbon dioxide liberated in any determination (*e.g.* from 30 mg of a pure uronic acid) does not exceed 4 ml; with a steady nitrogen flow-rate of 15 ml per min through an apparatus of internal volume 150 ml, the partial pressure of carbon dioxide, even at the time of maximum rate of production, is very small. Although the recovery of all carbon dioxide liberated from a carbonate had been carefully verified[20] during the development of the apparatus, the extent of the retention of carbon dioxide by the apparatus was nevertheless investigated.

Labelled barium carbonate was weighed in a small glass bucket and placed in a special reaction flask fitted with a side-arm dropping-funnel for addition of acid (*cf.* ref. 20). The ground-glass joint of this flask was joined to that of a standard decarboxylation apparatus[20] which, immediately previously, had been used in a routine determination so that the surfaces of its cooling coils were coated with the normal equilibrium amount of water. After scavenging the assembled apparatus

* We are grateful to Dr. R. Scott, Biophysics Dept., University of Edinburgh, for making this cell and for placing at our disposal the counting equipment used in these experiments (see *J. Sci. Instr.*, 1961, **38**, 31).

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with nitrogen in the usual way,[20] acid was added from the dropping funnel. The experimental conditions were therefore reproduced in all respects except that more dilute acid was used. The stream of flow-gas + reaction products was passed through the counting cell into the standard titration-cell[20] charged with baryta. Table I shows the results of a typical experiment in which the

TABLE I. RECOVERY OF CO_2 FROM $BaCO_3$-^{14}C

Time,* *min*	Total count	Count per min	Dead-time† correction	∴ Corrected count per min	∴ True count per min	Total corrected count
0		47 (background)				
5	3,400	3,539	85	3,624	3,577	3,871
10	40,000	9,900	701	10,601	10,554	42,373
20	196,500	21,000	4,454	25,454	25,407	223,139
30	331,600	8,300	487	8,787	8,740	327,341
40	380,000	2,700	49	2,749	2,702	422,070
60	398,980	300	1	301	251	440,265
90	—	72	—	72	25	—

* Measured from time of switching on heater; reflux began 10 min later.
† From tables.

weight of labelled barium carbonate taken was 7·34 mg, and the weight of carbon dioxide found, as determined by the usual titration-cell procedure, was equivalent to 7·41 mg of barium carbonate. In another experiment, 3·26 mg of labelled barium carbonate were mixed with 10·50 mg of AnalaR barium carbonate; the cell titration gave carbon dioxide equivalent to 13·94 mg of barium carbonate; the initial background count was 54 and the true count per min, after 1 hr, was 11.

Procedure for decarboxylation experiments

The labelled uronic acid was weighed in a small glass bucket and added to the reaction-flask.

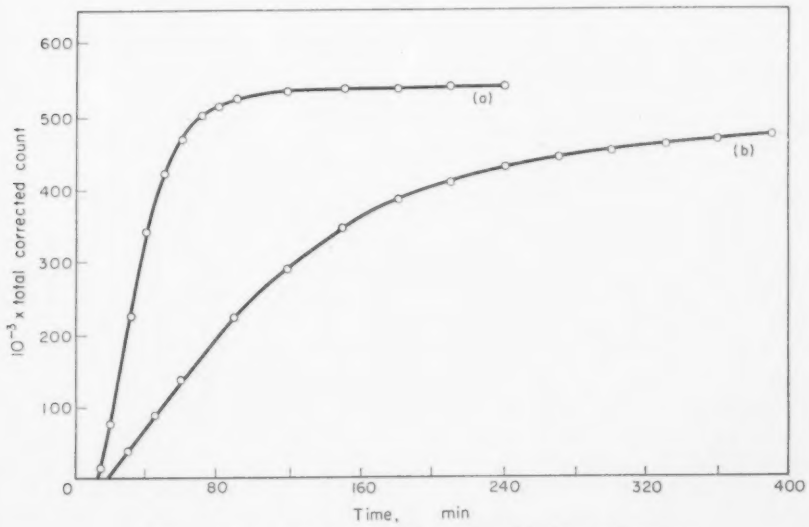

FIG. 1.—Rate of liberation of radioactive CO_2 from glucuronate.
Curve (*a*): 19% (w/w) aq. hydrochloric acid
Curve (*b*): 12% (w/w) aq. hydrochloric acid

The apparatus, reaction conditions, and reagents were all as previously described.[20] The stream of carrier-gas + reaction products was passed *via* the counting cell into the standard titration-cell.[20] Experiments were made with both 12% and 19% (w/w) aq. hydrochloric acid. For convenience, the time at which the heater was switched on was taken as arbitrary zero.

RESULTS

Typical results for the decarboxylation of potassium-D-glucuronate-6-^{14}C (7·10 mg) in 19% (w/w) hydrochloric acid are shown in Table II; the counts quoted are corrected for initial background and for detector dead-time. Table III shows the results obtained when a sample (6·05 mg) was decarboxylated in 12% (w/w) aq. hydrochloric acid.

When the total corrected counts given in Tables II and III are plotted against the quoted values for time, (see Fig. 1) extrapolation of the reaction-curves shows the true zero-time of the reactions to occur at 14 and 18 min respectively. (This arises from two factors: (*a*) Reflux began about 10 min after the heater was switched on; evolution of carbon dioxide begins, however, before reflux temperature is reached. (*b*) For a flow rate of 15 ml per min and a decarboxylation apparatus of volume approx. 150 ml, about 10 min must elapse before the first traces of carbon dioxide liberated are swept through the counting apparatus.)

TABLE II. DECARBOXYLATION IN 19% (W/W) HYDROCHLORIC ACID

Time,* *min*	True count† per min	Total corrected count†	% moles CO_2 per mole glucuronate
0	54 (background)	0	
10	150	455	
15	6,960	15,472	
20	14,301	76,061	
30	13,821	225,346	45
40	10,089	342,793	
50	6,741	420,687	
60	1,161	470,760	
70	2,176	501,370	86
80	1,064	516,229	
90	518	523,367	90
120	173	532,227	
150	96	536,038	92
180	86	538,698	
210	56	540,660	93
240	52	542,442	
270	54	544,220	—

* As in Table I.
† Deduced as shown in Table I.

After correction of the times shown in Table II to the true zero-time of the reaction, calculation of the rate constant by Guggenheim's method[25] gave $k_1 = 7{\cdot}4 \times 10^{-4}$ sec^{-1} for 19% acid. After corresponding correction of the times shown in Table III, subsequent calculation[25] gives the rate constant for 12% acid as $k_1 = 1{\cdot}6 \times 10^{-4}$ sec^{-1}.

DISCUSSION

The barium carbonate experiments indicated that recovery of the carbon dioxide *liberated in a rapid reaction* is quantitative, to within 1%, in 1 hr. This period was independent of the sample-weight, and there was no prolonged retention of carbon dioxide in the apparatus.

TABLE III. DECARBOXYLATION IN 12% (W/W) HYDROCHLORIC ACID

Time,* *min*	True count† per min	Total corrected count†	% moles CO_2 per mole glucuronate
0	70 (background)	0	
15	291	1,599	
30	3,724	36,680	
45	3,409	88,128	
60	3,204	137,183	40
90	2,472	221,931	
120	2,163	289,088	
150	1,752	344,723	
180	1,140	387,774	
210	421	407,041	
240	623	427,498	88
270	482	444,000	91
300	361	456,309	93
330	220	464,885	
360	180	470,887	97
390	80	473,653	

*, †, As in Table II.

Table II shows that, for 19% acid, the true count per minute reaches a low steady value after 210 min (200 min from start of reflux). This is therefore the time required *for complete decarboxylation* with the present apparatus and reaction conditions. In terms of the total carbon dioxide evolved, however, (*i.e.* labelled + unlabelled) the yield equivalent to the percentage purity of the labelled material is obtained in 140–160 min from start of reflux (*cf.* ref. 20). This is the correct analytical reaction time; although decarboxylation is only 98–99% complete, the total yield of carbon dioxide includes >1% from side reactions. Generally, the correct reaction-time may vary within small limits (say ±10 min) depending on the apparatus design and also, to a small extent, on the flow-rate.

This may explain *small* differences from the reaction-times quoted by certain previous workers. It will not, however, explain the wide range of reaction-times covered when all previous recommendations are considered. The undesirable use of an oil-bath, maintained at 145°, to sustain a reflux temperature of 109° has already received comment.[20]

A similar consideration of the results in Table III shows that, under our conditions, the analytically correct time with 12% acid is 270–290 min from start of reflux. At that time, which agrees well with that proposed by several previous authors,[18,26,27] 97% of the total carbon dioxide comes from decarboxylation and 3% from side-reactions. It now appears that the widely differing times proposed by other authors[11,12,14,28] must be regarded as being in error.

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Although the rate of decarboxylation is much slower in 12% than in 19% acid, the rate of evolution of carbon dioxide from the side-reactions involving decarboxylation by-products is little altered (*cf.* ref. 18). Since the reflux period for 19% acid is only half that for 12%, the amount of spurious carbon dioxide formed is proportionately less. This finding is supported by results obtained[21] for the decomposition of non-uronic acid carbohydrate materials. It has been suggested[11,29] that the use of 19% acid introduces errors by increasing the amount of carbon dioxide produced in side-reactions: our results directly oppose these opinions.

In carbohydrate materials, uronic acid groups are generally present in the form of aldobiuronic acids. In these the glycosidic linkage is particularly stable to hydrolysis; a similar effect occurs in polyuronides. Experiments with 2-α-D-galacturonosido-L-rhamnose (isolated[30] from *Plantago arenaria*) and with trigalacturonic acid and alginic acid showed, however, that their decarboxylation curves in 19% hydrochloric acid were closely similar to that of the labelled glucuronate. It is therefore believed that the reaction-times established in this work are generally applicable to heterogeneous polysaccharide systems.

Acknowledgements—We thank Professor E. L. Hirst, C.B.E., F.R.S., for his interest in these studies, and the Department of Scientific and Industrial Research for a maintenance grant (to S. G.). We are grateful to Dr. R. Scott for valuable discussions. Financial support (for the purchase of ^{14}C compounds) from the Rockefeller Foundation is acknowledged.

Zusammenfassung—Die Reaktionszeiten zur vollständigen (99%) Decarboxylierung von Glucuronsäure, die am C_6 mit C-14 markiert ist sind 200 und 360 Minuten im 19 bzw. 12% ige (Gewichtsprozent) Salzsäure, vom Beginn des Rückflusses gerechnet. Die entsprechenden Geschwindigkeitskonstanten erster Ordnung sind $7{\cdot}4 \times 10^{-4}$ und $1{\cdot}6 \times 10^{-4}$ sec^{-1}. Da jedoch Kohlendioxyd durch gleichzeitig ablaufende Nebenreaktionen erzeugt wird, werden analytisch korrekte Ergebnisse (durch Fehlerkompensation) in kürzerer Zeit erhalten, nämlich 140–160 und 270–290 Minuten für die beiden oben genannten Säurekonzentrationen. Die in 19% iger Säure erhaltenen Resultate sind zuverlässiger, da Kohlendioxyd aus unkontrollierbaren Nebenreaktionen zu geringerem Grade entwickelt wird. Dies ist in Gegensatz zu manchen Publikationen.

Résumé—Les temps de réaction, pour la décarboxylation complète (99%) de l'acide glucoronique marqué en C_6 avec du carbone 14, sont respectivement 200 et 360 minutes, au commencement du reflux, pour des solutions aqueuses d'acide chlorhydrique à 19% et à 12% en poids. Les constantes de vitesse du premier ordre correspondantes sont $7{,}4 \times 10^{-4}$ sec^{-1} et $1{,}6 \times 10^{-4}$ sec^{-1}. A cause de la réduction simultanée de l'anhydride carbonique par réactions secondaires, des résultats analytiques corrects sont donnés, par compensation des erreurs, dans des temps plus courts: 140–160 minutes pour l'acide à 19% et 270–290 minutes pour l'acide à 12%. Les résultats indiquent aussi que l'utilisation de l'acide à 19% réduit au minimum l'erreur provenant de la production d'anhydride carbonique dans les réactions secondaires, contrairement aux opinions publiées.

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THE DETERMINATION OF RHENIUM IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—Neutron-activation analysis has been applied to the determination of rhenium in rocks. Samples of the powdered rocks together with standards were irradiated in the Harwell Pile BEPO. Rhenium was separated from the irradiated rocks by a radiochemical procedure, using carriers, precipitations and solvent extractions. Radiochemically pure ^{186}Re was counted, and the chemical yield determined gravimetrically.

Results for the rhenium contents of the standard rock samples Gl and Wl are reported. The ultimate sensitivity of the analytical method is *ca.* 5×10^{-5} ppm Re.

THE abundance of rhenium in rocks is extremely low and a very sensitive method of analysis is necessary if the geochemical behaviour of the element is to be established satisfactorily. The present paper reports a neutron-activation procedure for the determination of rhenium in rocks, with an ultimate sensitivity of *ca.* 5×10^{-5} ppm of Re.

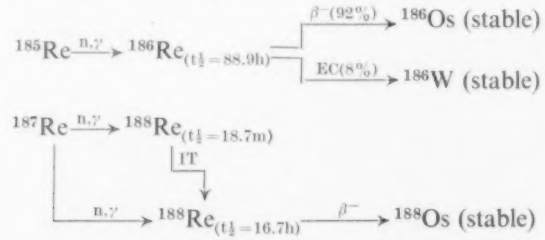
Goldberg and Brown[1] have previously employed neutron-activation in determining rhenium in some iron meteorites, and they report values ranging from 0.25 to 1·4 ppm. of Re. Herr and co-workers[2,3] have used the method to determine rhenium in molybdenites and iron meteorites.

Rhenium can be classified from the geochemical point of view as a siderophile element and concentrations found in rocks are generally much lower than those found in molybdenite and iron meteorites.[4,5]

NEUTRON-ACTIVATION OF RHENIUM

Naturally occurring rhenium consists of two isotopes, ^{185}Re (abundance 37·07%) and ^{187}Re (abundance 62.93%). The latter isotope is radioactive,[3] decaying by β^--emission with a half-life of $6{\cdot}3 \times 10^{10}$ years to ^{187}Os. This decay may be of use for determining geological ages.[3,6]

On irradiation with neutrons of thermal energies, rhenium gives rise to radionuclides by the following nuclear sequences



Isotopic thermal neutron-activation cross-sections, σ, for the nuclear reactions[7] are

$$^{185}\mathrm{Re}(n,\gamma)^{186}\mathrm{Re}\ \sigma = 100 \text{ barns}$$

$$^{187}\mathrm{Re}(n,\gamma)^{188}\mathrm{Re}\ \sigma = 75 \text{ barns.}$$

The radionuclide ^{186}Re was used in the present study. Its decay scheme[8] is shown in Fig. 1.

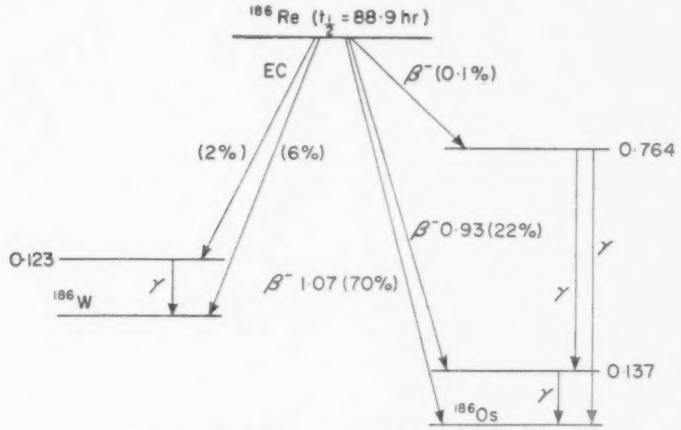


FIG. 1. Decay scheme for ^{186}Re, energies in MeV.

EXPERIMENTAL

Irradiation

Samples of the powdered rocks, about 1 g, were accurately weighed and sealed in 6-mm internal-diameter silica irradiation tubes. Standards were prepared by weighing out *ca.* 0·1-ml aliquots of a dilute standard solution of rhenium (15 mg of Re/litre) into 4-mm internal-diameter silica tubes, which were then sealed. Samples and standards were packed with silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron-irradiation. Irradiations were for periods of 2 weeks in the nuclear reactor BEPO with a thermal neutron flux of 10^{12} neutrons/cm^2/sec.

Extreme care was taken to avoid any chance of contamination of the samples before irradiation.

Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were left to "cool" for 1 day and then were assayed radiochemically for ^{186}Re. A procedure involving carriers, precipitation, and solvent extraction[9] was used for the separation of rhenium from the irradiated rock samples.

Preparation and standardisation of rhenium carrier

Dissolve 8·1 g of $KReO_4$ (Johnson Matthey and Co.) in 1 litre of H_2O.

Pipette exactly 5 ml of the carrier solution into a 100-ml beaker. Add 20 ml of 0·6*M* NaCl and warm to 60°. Then add an excess of 0·05*M* tetraphenylarsonium chloride, $(C_6H_5)_4$ AsCl. Stir the mixture, and allow to stand overnight. Filter through a porous porcelain crucible, and wash several times with ice-water. Dry at 110° and weigh as $(C_6H_5)_4AsReO_4$.[10]

Radiochemical separation procedure for rhenium in rocks

Step 1: Remove the irradiation tubes from the can, open them at the constriction, and transfer the powdered rock samples quantitatively to nickel crucibles. To each add 4 g of powdered Na_2O_2 and mix thoroughly. Finally, cover the mixture in each crucible with a layer of Na_2O_2 and heat in an electric muffle furnace at 500° for 10 min. Remove the crucibles from the furnace and quickly cool

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them by immersing their outside walls in a beaker of water. Transfer the cake from each crucible to a 150-ml beaker covered with a watch-glass. Dissolve the melt carefully in a small quantity of H_2O and add 2 ml of Re carrier. Digest for a few min on a steam-bath. (*Note a*)

Step 2: Add conc. HCl to the solution until the final HCl concentration is *ca.* 3*M*. Centrifuge and transfer the supernate to a clean 50-ml glass centrifuge tube. Heat the solution nearly to boiling on a steam-bath (*Note b*), and saturate with H_2S for some min with continued heating (*Note c*). Centrifuge and discard the supernatant solution.

Step 3: Wash the precipitate of Re_2S_7 with *ca.* 10 ml of H_2O and dissolve by gently heating with 1 ml of conc. HNO_3. Add 10 ml of conc. HBr and carefully evaporate nearly to dryness (*Note d*).

Step 4: Take up the residue completely in 20 ml of *M* H_2SO_4. Extract rhenium by agitating with a 15-ml portion followed by two 5-ml portions of benzyl alcohol. Separate and combine the organic (upper) layers. Wash the organic extract twice with 10-ml portions of 5*M* NaOH. Combine the alkaline washes and discard the organic phase (*Note e*).

Step 5: Agitate the alkaline aqueous solution with a 15-ml portion and then with two 5-ml portions of methyl ethyl ketone. Separate the organic (upper) layers, combine them together and wash them with 10 ml of 5*M* NaOH. Finally separate the organic phase into a clean 50-ml glass centrifuge tube and evaporate off the ketone in a water-bath. (*Note f*).

Step 6: Dilute the residue to 20 ml with H_2O, add 1 ml of Fe^{III} carrier (2 mg of Fe/ml as $FeCl_3$ in v. dil. HCl), heat, and add NH_4OH until $Fe(OH)_3$ is precipitated. Centrifuge, and discard the precipitate.

Step 7: Heat the supernatant solution and add 1 ml of 0·05*M* $(C_6H_5)_4$ AsCl to precipitate $(C_6H_5)_4$ $AsReO_4$. Wash three times with 5 ml of H_2O. Slurry the precipitate with a little H_2O on to a weighed aluminium counting tray (A.E.R.E. cat. no. 4–3/1068). Dry at 110° for 10 min and weigh to determine the chemical yield.

Notes

(*a*) Operations should be quantitative until exchange with carrier has been brought about.

(*b*) Hydrochloric acid solutions containing Re^{VII} should not be boiled, since perrhenic acid is appreciably volatile in vapours containing HCl.

(*c*) The Re_2S_7 may precipitate slowly.

(*d*) Do not take completely to dryness. ReO_3Br boils at 163°.

(*e*) Distribution ratios,

$$D = \frac{\text{(total concentration of rhenium in the organic phase)}}{\text{(total concentration of rhenium in the aqueous phase)}},$$

for the solvent extraction stages in the radiochemical procedure are as follows:

benzyl alcohol–*M* H_2SO_4	D = 2·9
benzyl alcohol–5*M* NaOH	D = 0·07
methyl ethyl ketone–5*M* NaOH	D = 4·3.

These values were measured using ^{186}Re as tracer.

(*f*) Evaporate the ketone at a controlled temperature of 70–75° with air-sparging.

Treatment of the irradiated rhenium standards

At a convenient time open the silica tubes containing the Re standards. Using a transfer pipette drawn out to a fine point, transfer the Re solution quantitatively to a 100-ml calibrated flask and rinse thoroughly with H_2O. Dilute to the mark with H_2O. Transfer a suitable measured aliquot, depending on the amount of Re to be expected in the sample, to a 50-ml centrifuge tube. Add 2 ml of Re carrier and 20 ml of 0.6*M* NaCl. Precipitate $(C_6H_5)_4$ $AsReO_4$, mount, dry and weigh it as decribed in Step 7 of the procedure for rock samples.

Counting of the $(C_6H_5)_4$ $AsReO_4$ *precipitates*

In the present work the final precipitates of $(C_6H_5)_4$ $AsReO_4$ from samples and standards were counted with a thin end-window Geiger-Müller counter (EHM 2/S). An aluminium absorber (26.9 mg/cm²) was inserted between each source and the detector. All measured activites were corrected for paralysis, background, and chemical yield.

Decay measurements on the final precipitates were performed. After *ca.*100 hr from the end of neutron irradiation the decay curves were straight lines corresponding with the half-life of ^{186}Re. Extrapolation of the straight line portions of these curves to zero time, or to any arbitrary time, gave an activity reading for samples and standards from which the rhenium content of the original material could be found from the relationship

$$\text{Weight of Re in a sample} = \text{Weight of Re in a standard} \times \frac{\text{Corrected counting rate of the sample}}{\text{Corrected counting rate of the standard}}.$$

Aluminium absorption measurements on final precipitates gave a value of 1.08 Mev for the maximum β^--energy (the literature value[8] for ^{186}Re is 1.072 Mev). Additional confirmation that ^{186}Re was the only radionuclide being assayed was obtained by measuring the γ-ray spectra of final precipitates with a NaI (T1) crystal scintillation spectrometer. Typical spectra are shown in Fig. 2.

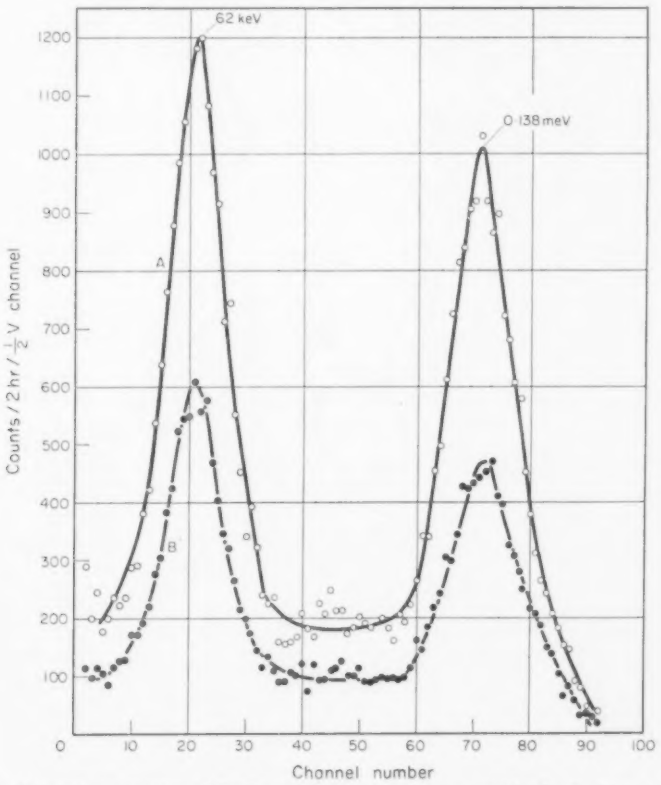

FIG. 2. Gamma-ray spectra of final precipitates: A, from a standard; B, from a rock sample.

RESULTS

In Table I are shown results of neutron-activation analyses of rhenium in the standard granite G1 from Westerley, Rhode Island, and in the standard diabase W1 from Centreville, Virginia. Uniform specimens of these rocks have been widely distributed by the U.S. Geological Survey as standards for both major and minor constituents in igneous rocks.[11,12] Owing to the extremely low rhenium contents and the possibility of contamination, *e.g.* in the initial grinding of the rock samples, it is felt that the results should be taken as representing maximum values.

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Analytical results for rhenium in other rocks will be published elsewhere. It is of interest to note that the values of 0·010, 0·012 ppm were obtained for the rhenium content of Specpure precipitated silica (Johnson Matthey and Co.)

Table I. Rhenium contents of the standard granite G1 and the standard diabase W1 determined by neutron-activation analysis

G1, *ppm*	W1, *ppm*
0·0005	0·0007
0·0008	0·0006
0·0006	0·0008
0·0007	0·0006
0·0008	0·0008
0·0006	
Av. 0·0007	Av. 0·0007

The analysis procedure described in the present work was tested by adding 0·245 μg of rhenium to a 1-g sample of rock containing 0·0003 ppm of the element and determining the added rhenium by neutron-activation; the rhenium found was 0·243 μg.

DISCUSSION

In the determination of rhenium by neutron-activation, consideration must be given to possible interference resulting from other elements.

The radiochemical procedure developed in the present work does not provide a separation of technetium from rhenium. However, the radionuclide ^{99m}Tc ($t_{\frac{1}{2}}$ 6 hr; IT, 0·0018 MeV; γ, 0·1403 MeV) may be produced in the neutron-irradiation of rocks by the following processes:

$$^{98}\mathrm{Mo}(n,\gamma)^{99}\mathrm{Mo} \xrightarrow[t_{\frac{1}{2}} = 66\ \mathrm{hr}]{\beta^-} {}^{99m}\mathrm{Tc}$$

$$^{98}\mathrm{Tc}(n,\gamma)^{99m}\mathrm{Tc}$$

$$^{99}\mathrm{Tc}(n,n')^{99m}\mathrm{Tc}$$

$$^{99}\mathrm{Ru}(n,p)^{99m}\mathrm{Tc}$$

Any interference caused by the formation of ^{99m}Tc should be apparentfrom decay curves measured on the final precipitates from rock samples. In the present study* there was no need to separate technetium chemically but this could have been done, *e.g.* by anion-exchange.[13,14]

Attention must also be given to the possibility of formation of rhenium radionuclides from tungsten by the sequences

$$^{184}\mathrm{W}(n,\gamma)\ ^{185}\mathrm{W} \xrightarrow[t_{\frac{1}{2}} = 74\ \mathrm{d}]{\beta^-} {}^{185}\mathrm{Re}(n,\gamma)^{186}\mathrm{Re} \qquad (1)$$

$$^{186}\mathrm{W}(n,\gamma)\ ^{187}\mathrm{W} \xrightarrow[t_{\frac{1}{2}} = 24\mathrm{hr}]{\beta^-} {}^{187}\mathrm{Re}(n,\gamma)^{188}\mathrm{Re}\ . \qquad (2)$$

* The aluminium absorber employed in the radiometric assays would absorb conversion electrons from the IT (e/γ very large) and γ(e/γ 0.11) decay of ^{99m}Tc.

The abundance of tungsten in igneous rocks has been quoted[4] as 1·5–69 ppm (activation analyses[15] have shown that G1 contains 0·12 ppm of tungsten and W1 contains 0·43 ppm). It may be shown by calculation[16,17] that under the neutron-irradiation conditions employed in the present work the ^{188}Re activity produced from 50 ppm of W in a rock by sequence (2) corresponds to that produced from 0·00075 ppm of rhenium. Because of this possible interference, ^{188}Re has been allowed to decay away and only ^{186}Re has been assayed in the present work. For a rock containing 50 ppm of W the ^{186}Re activity produced by sequence (1) corresponds to that from only $3{\cdot}4 \times 10^{-6}$ ppm of rhenium.

Rhenium-186 could also be produced from osmium by the nuclear reaction

$$^{186}\mathrm{Os(n,p)}^{186}\mathrm{Re}\ . \qquad (3)$$

This reaction could occur with fast neutrons of which there is a flux of $1{\cdot}6 \times 10^{11}$ per cm^2 per sec under the irradiation conditions employed[18] in BEPO. However, since osmium is unlikely to occur in a rock to an extent exceeding 0·01 ppm and the cross-section for reaction (3) with the pile distribution of neutrons calculated by the method of Hughes[19] is only 0·19 millibarns, possible interference from this source may be ignored.

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The authors wish to record their gratitude to Dr. R. G. Monk for helpful discussion.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Rhenium in Gesteinen herangezogen. Gesteinsproben (gepulvert) wurden zusammen mit Standardproben in der Harwell-Pile BEPO bestrahlt. Rhenium wurde sodann mittels radiochemischer Methoden unter Heranziehung von Trägern, sowie Fällung und Extraktion isoliert und ^{186}Re gezählt. Ergebnisse für den Rheniumgehalt von Gesteinsstandard G1 und W1 werden mitgeteilt. Die Empfindlichkeit der Methode ist etwa 5×10^{-5} ppm Re.

Résumé—Les auteurs ont appliqué l'analyse par activation de neutrons au dosage du rhénium dans les roches. Des échantillons de roches pulvérisées, ainsi que des étalons, ont été irradiés dans la pile BEPO de Harwell. Le rhénium a été séparé des roches irradiées par une méthode radiochimique utilisant entraineurs, précipitations et extractions par solvant. ^{186}Re radiochimiquement pur a été compté, et le rendement chimique a été déterminé par gravimétrie. Les valeurs de la teneur en rhénium des échantillons de roches étalon G_1 et W_1 sont données. La sensibilité maximale de la méthode d'analyse est environ 5.10^{-5} p.p.m. de rhénium.

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SHORT COMMUNICATIONS

Sur un principe de colorimétrie en milieu non aqueux—III L'emploi du chlorure de *p*-nitrophénylazobenzoyle pour le dosage des amines primaires et secondaires

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LE CHLORURE de *p*-nitrophénylazobenzoyle a été précédemment retenu pour caractériser les alcools.[1] Selon nos essais, l'emploi de ce réactif pour la colorimétrie des amines est possible en milieu non aqueux, sur le principe que nous avons précédemment énoncé.[2] On parvient ainsi, dans le diméthylsulfoxyde, à développer une coloration sans isolement préalable de l'amide formé, ni élimination de l'excès de réactif.

Après acylation de l'amine en dioxane par le chlorure de *p*-nitrophénylazobenzoyle, l'addition d'hydroxyde de benzyl-triméthylammonium puis d'eau oxygénée en diméthylsulfoxyde conduit à une coloration rouge (510 mμ) qui n'est pas observée en absence d'amine. La réaction est fournie par les amines primaires et secondaires et, la loi de Beer étant satisfaite, des dosages sont possibles sur des prises d'essais de l'ordre du centième de milligramme (Tableau I).

TABLEAU I

Amines dosées	Prise d'essai, μg, pour obtenir une densité optique de 0,3 en cuve de 1 cm	
Amines aliphatiques		
Benzylamine	9,5	(à 510 mμ)
Butylamine	4,5	(à 510 mμ)
Ethylamine	3,0	(à 510 mμ)
Propylamine	4,5	(à 510 mμ)
Dibenzylamine	35	(à 500 mμ)
Dibutylamine	12	(à 495 mμ)
Diéthylamine	6	(à 495 mμ)
Dipropylamine	14	(à 495 mμ)
Amines aromatiques		
Aniline	25*	(à 510 mμ)
Méthylaniline	16	(à 510 mμ)

* Dans ce cas, la densité optique est égale à 0,11.

Les amines tertiaires et les alcools ne sont pas révélés dans les conditions opératoires ici décrites; leur présence n'apporte donc pas de gêne au dosage des amines réactives.

PARTIE EXPERIMENTALE*

Réactifs

Chlorure de p-*nitrophénylazobenzoyle*[1] à 0,01 pour cent dans le dioxane.

Solution préparée extemporanément et refroidie *d'hydroxyde de benzyltriméthylammonium* à 0,05 pour cent dans le diméthylsulfoxyde, obtenue par dilution par 20 volumes de solvant d'une solution aqueuse à 1 pour cent de l'hydroxyde d'ammonium.

Peroxyde d'hydrogène à 0,5 volume, obtenu en diluant 0,5 cm^3 d'eau oxygénée concentrée (perhydrol à 100–110 volumes) à 100 cm^3 avec du diméthylsulfoxyde.

Mode opératoire

La prise d'essai de l'amine étant en solution dans 2 cm^3 de dioxane, on ajoute 1 cm^3 de solution de chlorure d'azoïque. Après repos pendant 5 minutes à température ordinaire, on ajoute 2 cm^3 de solution d'hydroxyde de benzyltriméthylammonium dans le diméthylsulfoxyde, puis 0,5 cm^3 de solution de peroxyde d'hydrogène dans le même solvant. Après dix minutes de repos, lecture par rapport à un témoin sans amine.

Centre de Recherches Roussel-Uclaf JAROSLAV BARTOS
Paris, France

Résumé—Les tests d'identification en milieu non aqueux qui ont été précédemment décrits (*Talanta*, 1960, **5**, 216; 1961, **8**, 556) ont été étendus au dosage des amines primaires et secondaires sous forme d'amides *p*-nitrophénylazobenzoïques. Après acylation, on développe directement la coloration dans le diméthylsulfoxyde. Les prises d'essais sont de l'ordre de 0·01 mg.

Summary—The qualitative tests in non-aqueous medium which have been described previously (*Talanta* 1960, **5**, 216; 1961, **8**, 556) have been extended to the determination of primary and secondary amines as the *p*-nitrophenylazobenzoic amides. After acylation, the colour is developed directly in dimethylsulphoxide. The samples are of the order of 0·01 mg.

Zusammenfassung—Die qualitativen Prüfungen in nicht-wässerigem Medium die bei früherer Gelegenheit beschrieben wurden (*Talanta*, 1960, **5**, 216; 1961, **8**, 556), wurden jetzt weitergeführt, so dass sie auch die Bestimmung der primären und secundären Amine einschleissen, wie die *p*-Nitrophenylazobenzo-amide. Nach der Acetylation, die Färbung wird in Dimethylsulphoxyd direkt entwickelt. Die Proben sind von der Grössenordnung von 0.01 mg.

REFERENCES

[1] Voir en particulier E. Hecker, Chem. Ber., 1955, **88**, 1666.
[2] M. Pesez et J. Bartos, *Talanta* 1960, **5**, 216; 1961, **8**, 556.

* avec Mlle G. Clement

The use of ruthenium tetroxide as a catalyst in redox titrations

(*Received* 6 *April* 1961. *Accepted* 4 *May* 1961)

INTRODUCTION

THE oxidation of arsenious oxide by ceric sulphate in an acid medium is probably the classic example of a reaction that needs to be catalysed in order that it may proceed at a rate that renders it useful as an analytical procedure. Iodine monochloride is occasionally recommended as a catalyst[1] but a solution of osmium tetroxide in sulphuric acid is the reagent that finds almost universal application.[2,3]

In a recent review article on oxidations in alkaline media[1] it would appear that the desired catalytic effect is provided exclusively by osmium tetroxide. In view of the chemical similarity between osmium and ruthenium tetroxides, it was thought likely that a solution of ruthenium tetroxide in sulphuric acid could equally well be employed as a catalyst, and it was considered worthwhile to study reactions in both acid and alkaline media. The titration of arsenious oxide with ceric sulphate and of sulphite with ferricyanide were chosen as being representative of reactions in acid and alkaline media respectively, the end-point being determined by both potentiometric and visual methods where applicable.

EXPERIMENTAL

Apparatus

Potentiometric readings were taken with a "Pye" Universal pH-meter using a platinum/saturated-calomel electrode system.

Reagents

Ceric Sulphate, approx. 0·1N: Dissolve 56 g of ceric ammonium nitrate (AnalaR Grade) in 200 ml of water and add excess 5*N* ammonia solution until precipitation is complete. Filter and wash well with water. Dissolve the precipitate in 400 ml of warm 4*N* sulphuric acid, allow to cool and dilute to 1 litre with water.

Arsenious oxide, 0·1N: Dissolve 2·473 g of arsenious oxide (AnalaR Grade) in 20 ml of 10% w/v sodium hydroxide, dilute to about 200 ml, and add dilute hydrochloric acid until the solution is just acid (litmus). Add 2 g of sodium bicarbonate, transfer the solution quantitatively to a 500 ml calibrated flask, and dilute to the mark with water.

Ruthenium tetroxide solution, saturated: Shake 0·5 g of ruthenium tetroxide with 50 ml of 0·1*N* sulphuric acid at room temperature until no more tetroxide dissolves.

"Ferroïn" solution: Obtained from Hopkin and Williams Ltd., Chadwell Heath, Essex, England.

Sodium sulphite, 0·1N: Dissolve 3·152 g of $Na_2SO_3.7H_2O$ (AnalaR Grade) in water and dilute to 250 ml in a calibrated flask. This solution should be renewed every 2 days.

Potassium ferricyanide, 0·1M: Dissolve 8·231 g of $K_3[Fe(CN)_6]$ (AnalaR Grade) in water and dilute to 250 ml in a calibrated flask. This solution should not be kept for more than 1 week.

1. *Titration of arsenious oxide with ceric sulphate in the presence of ruthenium tetroxide*

Aliquots (25 ml) of 0·1*N* arsenious oxide solution were diluted with 50 ml of dilute sulphuric acid (1 + 5), and 2 drops of "Ferroïn" indicator solution were added, followed by varying amounts of ruthenium tetroxide solution. Ceric sulphate solution was added until a colour change was observed. The results are given in Table I and although these indicate that a good end-point could be obtained, the amount of ruthenium tetroxide solution used appeared to be very critical. Using a potentiometric

TABLE I.—TITRATION OF ARSENIOUS OXIDE WITH CERIC SULPHATE IN THE PRESENCE OF RUTHENIUM TETROXIDE

RuO_4 taken, *ml*	Titre, *ml*	Remarks
0·1	25·1	Reaction very slow. End-point difficult to detect.
0·3	24·8	Reaction very slow. End-point difficult to detect.
0·5	24·25	Reaction very slow. End-point difficult to detect.
0·8	24·1	Good end-point. No fading.
0·9	23·8	Good end-point. No fading.
1·0	24·05	Good end-point. No fading.
1·0	23·2	Good end-point. No fading.
1·5	22·5	Colour change indistinct.
2·0	21·4	Colour change indistinct.

method of end-point detection, reproducible results could be obtained, but the end-point was inferior to that using osmium tetroxide. Furthermore, it was found that the catalytic effect of the solution depended on its age; thus, a freshly prepared solution showed no catalytic properties, whereas after

ageing for 16 hr, the solution was strongly active. On standing for 2 days, however, the catalytic activity was considerably diminished. No explanation is offered for this behaviour but it must be concluded that ruthenium tetroxide has no advantage as a catalyst in the Ce^{+4}/As^{+3} system.

2. *Titration of sulphite with ferricyanide in the presence of ruthenium tetroxide*

Various sample volumes of 0·1*N* sodium sulphite solution were added to 200 ml portions of 5*N* sodium hydroxide solution. After heating to 65–70°, 6 drops of ruthenium tetroxide solution were added, and the mixture was titrated with 0·1*M* potassium ferricyanide solution, with continuous stirring. The course of the titration was followed by a valve millivolt-meter using a platinum/saturated-calomel electrode system. In addition, it was necessary to employ a "backing-off" potential, in order to bring the millivolt readings within the optimum range of the millivolt-meter.

It was found that the catalytic action of ruthenium tetroxide was slower than that of osmium tetroxide, causing the initial "jump" of the millivolt-meter needle to take some time to return to a stable reading. However, the following technique was found to give very satisfactory results:

The potassium ferricyanide solution was added from a burette in small portions, the initial "jump" of the needle being followed by an immediate but slow fall of the meter reading. On approaching the end-point, the decrease in millivolts was less immediate and the end-point was judged to have been reached when the meter reading remained steady after the addition of ferricyanide.

This technique was rapid and the results were easily reproducible. The catalyst solution, although yielding a black precipitate after a very short time, was still effective even on standing for at least 2 weeks.

Typical results obtained by this method are given in Table 2.

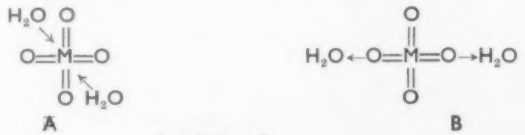
TABLE II.—TITRATION OF SODIUM SULPHITE SOLUTION WITH POTASSIUM FERRICYANIDE SOLUTION IN THE PRESENCE OF RUTHENIUM TETROXIDE

Sulphite taken, *ml*	Sulphite found, *ml*
5·0	4·9
5·0	4·9
5·0	4·9
5·0	4·8
4·0	3·8
3·0	3·1
3·0	2·8
3·2	3·15
2·0	1·85
2·0	2·0

From these figures it may be concluded that ruthenium tetroxide can satisfactorily replace the corresponding osmium analogue and is to be preferred in view of its relative non-toxicity and its lower cost.

DISCUSSION

The formulation of ruthenium tetroxide and osmium tetroxide in aqueous solution is open to discussion. It has been suggested that at least two possibilities exist[5] as shown in A and B, although it is admitted that no experimental evidence is available to support either configuration.



In addition, conflicting results on the measurement of the bond lengths of both tetroxides appear to have been obtained. The evidence offered by Brockway[6] suggests that the four bonds are of equal length, whereas Braune and Stute[7] claim that the bond lengths of both ruthenium and osmium tetroxides are in two equal pairs. Brockway's measurements would suggest formula A whereas Braune and Stute's results favour B.

The present work suggests that osmium tetroxide is a stronger catalyst than the ruthenium analogue and this may possibly be explained by assigning different structures to the two compounds. The stronger catalytic effect of osmium tetroxide would suggest the immediate availability of more oxygen atoms than in the case of ruthenium tetroxide. For this reason, formula A would appear to be more in keeping with the properties of osmium tetroxide and formula B would explain the weaker catalytic effect of the corresponding ruthenium compound.

Acknowledgement—The author wishes to thank The International Nickel Company (Mond) Ltd., for permission to publish this paper.

C. J. KEATTCH

The International Nickel Company (Mond) Limited
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London, England

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Summary—In the titration of arsenious oxide with ceric sulphate, ruthenium tetroxide can be used as a catalyst only if a potentiometric end-point is employed. On the other hand, in the oxidimetric determination of sulphite with ferricyanide, a potentiometric end-point is obligatory and the reaction is catalysed equally well by ruthenium or osmium tetroxide. The former is to be preferred on the grounds of its relative non-toxicity and lower cost.

Zusammenfassung—Bei der cerimetrischen Titration von Arsen(III) kann unter Verwnedung von Rutheniumtetroxyd der Endpunkt nur potentiometrisch indiziert werden. Bei der Bestimmung von Sulfit mit Ferricyanid jedoch wird der potentiometrische Endpunkt gleich gut von Ruthenium- wie auch Osmiumtetroxyd katalysiert. Die Rutheniumverbindung verdient den Vorzug, weil relativ ungiftig und billiger.

Résumé—Dans le titrage de l'oxyde arsénieux par le sulfate cérique, le tétroxyde de ruthénium ne peut être utilisé comme catalyseur, que si le point équivalent est déterminé par potentiométrie. D'autre part dans le dosage oxydimétrique du sulfite par le ferricyanure, le tétroxyde de ruthénium ou le tétroxyde d'osmium catalysent également bien la réaction si le point équivalent est déterminé par potentiométrie. Le premier doit être préféré à cause de son prix inférieur et du fait qu'il n'est relativement pas très toxique.

REFERENCES

[1] E. H. Swift and C. H. Gregory, *J. Amer. Chem. Soc.*, 1930, **52**, 901.
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[3] A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis.* Longmans, London, 2nd Ed., 1955, p. 303.
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[6] L. O. Brockway, *Rev. Mod. Phys.*, 1936, **8**, 260.
[7] H. Braune and K. W. Stute, *Angew. Chem.*, 1938, **51**, 528.

Talanta, 1961, Vol. 8, pp. 624 to 625. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

NMR and EPR Spectroscopy: by the NMR–EPR Staff of Varian Associates. Pergamon Press, Oxford, 1960. pp. 288. Price 80s. net

IN experimental fields developing as rapidly as nuclear and electron paramagnetic resonance, it is very difficult for either the newcomer in the field or even for the experienced investigator to keep in touch with new developments. Nuclear resonance effects were first detected in 1945 by Purcell, Torrey and Pound, and, simultaneously, by Bloch, Hansen and Packard. Since then, innumerable papers on the development and application of this technique to physical and chemical problems have appeared in the literature. To-day commercial spectrometers may be purchased, albeit at no small expense, from several sources so that there is hardly a university department of note which is not in possession of or is at least hoping to obtain one of these instruments. Electron resonance, although discovered earlier, is less well known, possibly because the techniques employed are less familiar, but also because its applications, important though they are, are less widespread than is the case with nuclear resonance.

The general unfamiliarity of the techniques in both fields, and the pace of development, have posed special problems. The book under review is the result of a praiseworthy attempt at a partial solution to some of them. Annually, Varian Associates, a firm prominent in the commercial development of resonance techniques, has arranged a gathering of workers from many countries and from a wide variety of disciplines to provide a meeting ground for keeping abreast with new developments. The contents of this book are summaries of the lectures and discussions at the 1959 meeting, approximately equal share being given to the two techniques. There are chapters on fundamental theory, high resolution NMR, operating fundamentals of both types of spectrometer, NMR as an analytical tool, integrating systems, and some interesting chapters on applications of the EPR technique, particularly in the biological field and in photochemistry. This is a useful book for the reader interested in a general introduction to resonance techniques and their applications, but it is directed mainly at the research worker who is already using instruments of the kind described, but is possibly not taking full advantage of the instrumental possibilities. For such a reader this book is a good investment. The general reader, on the other hand, may well think the price of 80s. in this country rather excessive.

R. C. PINK

Spot Tests in Organic Analysis. FRITZ FEIGL, 6th revised English Edition. Elsevier Publishing Company; D. Van Nostrand Co. Ltd., London 1960. Pp. xx + 675. 65s.

READERS of this journal will need no introduction to the work of Professor Feigl, whose distinguished contributions to modern analytical chemistry, summarised in *Talanta*, 1961, **8**, 170, were recognised by the first award of the Talanta Medal.

Compared with the 5th Edition, this edition increases by about 50% the number of tests described for functional groups and individual compounds, and the number of practical applications listed has nearly doubled. Tests are now given for recently developed materials such as plastics, synthetic rubbers and fibres, and for the modern pesticides based on phosphoric and thiophosphoric acids.

Only one chemical misprint was detected—OC_2H_3 for OC_2H_5 on p. 590, but several printing errors, such as "splitt" (p. 144), "access" for "excess" and "the" for "they" (p. 353), "alcholic" (p. 435), "onto" and "basid" (p. 444) can be found. In several places the text is quaintly non-chemical

in its wording as a result of too literal a translation; in particular, the frequent repetition of the clumsy heading "Test for . . . . . compounds by splitting off of . . . . . " becomes objectionable.

These minor criticisms over, this is a fine book. It should be classified as a "must" for every laboratory, regardless of its field of specialisation. Feigl does not present a mere description of procedures nor an empirical collection of recipes; he seeks a complete knowledge of the basic chemistry of the reactions involved in his spot-tests, because this is essential for the development of the conditions giving the maximum sensitivity and selectivity.

Only in a few instances, *e.g.* on pp. 321, 328, 380, 416–422, 469, are tests described for which the chemical reaction, or the constitution of the essential product, is unknown in the light of present knowledge: only occasionally are reactions plausibly presumed, without proof, to follow a certain course. Those persons who read the book from cover to cover, as a conscientious reviewer must—or should—do, will certainly learn a great deal of interesting chemistry. The book is clearly intended as a reference manual, however, and for this purpose it is excellently produced. The procedure for each test, and details of its specificity and sensitivity are clearly described; many references are listed. There are excellent indexes (42 pages) and a useful tabular summary (24 pages) classifying the various tests.

At 65s. this book is most reasonably priced.

D. M. W. ANDERSON

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Instability Constants of Complex Compounds: K. B. YATSIMIRSKII and V. P. VASIL'EV. Translated from the Russian by D. A. PATERSON. Translation Editor: R. H. PRINCE. Pergamon Press, London, 1960. pp. 218. 42s.

IN this little volume are collected the instability constants for 1381 complexes. The Tables, which have been compiled from data published up to 1954, and in some cases up to 1955/6, cover complexes of metal ions with 24 inorganic ligands and 75 organic ligands. An additional Table gives enthalpy and entropy as well as free energy changes for those few complex-formation reactions where this information is known. Each Table indicates the experimental method and conditions (ionic strength and temperature). The literature source for each instability constant is also included, as are supplementary references bearing on the same determination.

The Tables are preceded by four quite useful chapters (83 pages) dealing with definitions of the terms and functions commonly used in deriving instability constants from experimental data, the principles of the experimental methods themselves and their applicability and a brief discussion of the more important factors determining the stabilities of complexes. The importance of a knowledge of enthalpy and entropy factors in interpreting stability sequences is stressed, an area where Yatsimirskii himself has made major contributions.

On the dust-cover, it is claimed that this volume contains the first full collection of instability constants of complex compounds. While it undoubtedly represented the major compilation of its kind when first published in Russia, this was certainly no longer true at the time of issue (1960) of the translation in this country. The Tables of *Stability Constants* edited by Bjerrum, Schwarzenbach and Sillén, published by the Chemical Society in two parts (*Organic Ligands*, 1957 and *Inorganic Ligands*, 1958) is a far more comprehensive work. To take only one example, Part I of the Chemical Society publication lists the stability constants for the complexes of metal ions with 464 organic ligands as compared with 75 in the Tables under review, and similarly, in Part II, more than twice as many inorganic ligands are included as are here. A detailed comparison of the two sets of Tables shows that very few data are found in the present compilation that are not also found in the Chemical Society publications.

If this book had appeared in English translation four or five years ago it could have been recommended as being the best available collection of stability constants. Now, however, it must be admitted that those who find a need for reference data of this kind will still be better served by the earlier Chemical Society compilation.

S. M. NELSON

Talanta, 1961, Vol. 8, pp. 626 to 627. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Monday–Wednesday 18–20 *September* 1961: **Eighth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Mittwoch 18 *Oktober* 1961: Vortragstagung, Thema **Neuere Methoden der Stahl-Eisen-Analyse:** *Gesellschaft Deutscher Berg—und Hüttenleute, Deutsches Amt für Material—und Warenprüfung, und Fachverband "Analytische Chemie" der Chemischen Gesellschaft in der DDR.* Magdeburg.

Anmeldungen sind zu richten an das Deutsge Amt für Material—und Warenprüfung, Prüfdienststelle Metallurgie/Machinebau, Magdeburg (DDR), Große Steinernetischstraße 4.

Donnerstag 30 *November-Samstag* 2 *Dezember* 1961: Tagung, Thema **Reinstoffe in Wissenschaft in Technik;** *Chemische Gesellschaft in der DDR, Gesellschaft Deutscher Berg—und Hüttenleute, und die Physikalische Gesellschaft in der DDR.* Dresden.

Anmeldungen sind zu richten an die Chemische Gesellschaft in der DDR.

UNITED KINGDOM

Monday–Friday 11–15 *September* 1961: **Joint Conference on Mass Spectrometry:** *Institute of Petroleum, Hydrocarbon Research Group* and *A.S.T.M. Committee E–14.* Rhodes House, Oxford University.

Monday–Friday 9–13 *April* 1962: **Sixth Congress of the International Society for Fat Research.** Imperial College of Science and Technology, Prince Consort Road, London, S.W.7.

Amongst other subjects, the programme will cover new research techniques, including analytical methods.

Application forms for provisional registration of membership and for submission of papers may be obtained from the Congress Secretaries, Dr. F. BRADLEY and Dr. H. JASPERSON, 14, Belgrave Square, London, S.W.1.

The following new British Standard is announced in B.S.I. News:

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys: Part* 10: 1961: *Iron in ingot tin, tin-lead solders and white metal bearing alloys.* This specifies reagents required, and recommended methods of sampling and test procedure for the determination of iron in ingot tin, tin-lead solders and white metal bearing alloys having an iron content up to 0.03%. (Price 3s.)

Also announced is the following revised British Standard:

B.S. 769: 1961: *Methods for the analysis of butter.* This describes the preparation of sample and gives methods for the determination of moisture, curd and salt, salt, curd, fat, titratable acidity, volatile acids, iodine value, acidity in butter fat, saponification value, refractive index of butter fat, copper, iron, pH of butter serum. (Price 7s. 6d.)

UNITED STATES OF AMERICA

Tuesday–Friday 5–8 *September* 1961: **Eleventh National Chemical Exposition:** *American Chemical Society, Chicago Section.* International Amphitheatre, Chicago, Ill.

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Wednesday–Friday 6–8 *September* 1961: **Joint Nuclear Instrumentation Symposium:** *Instrument Society of America, Institute of Radio Engineers* and *American Institute of Electrical Engineers.* North Carolina State College, Raleigh, N.C.

Monday–Friday 11–15 *September* 1961: **Sixteenth Annual Meeting and Fall Instrument-Automation Conference and Exhibit:** *Instrument Society of America.* Biltmore Hotel (Conference) and Memorial Sports Arena (Exhibit), Los Angeles, Calif.

Monday–Friday 5–9 *March* 1962: **Thirteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *American Chemical Society, Pittsburgh Section* and *Spectroscopy Society of Pittsburgh.* Penn-Shearaton Hotel, Pittsburgh, Penna.,

Symposia on Chemical Analysis of Metals, Gas Chromatography, Raman Spectroscopy, Spectroscopic Studies of Polymers, and Vacuum Spectroscopy are planned. In addition, original papers on all phases of analytical chemistry and spectroscopy are invited.

Authors planning to submit papers should write to Dr. C. F. GLICK, Programme Chairman, The Pittsburgh Conference, Applied Research Laboratory, United States Steel Corporation, Monroeville, Penna. The absolute deadline for titles and abstracts is 16 *October*, 1961.

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Talanta, 1961, Vol. 8, p. 628. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Photometric Titrations—III: The Chelometric Titration of Cadmium in the Presence of Zinc: H. FLASCHKA and J. GANCHOFF. (30 *May* 1961).

Quantitative Paper Radiochromatography Using Tollens Reagent—I: The Application of ^{131}I for Radiometric Determination of Monosaccharides and Polyols: JANUSZ Z. BEER. (30 *May* 1961).

Volumetrische Bestimmung von Magnesium in Gegenwart von Calcium: R. FABREGAS, A. BADRINAS u. A. PRIETO. (30 *May* 1961).

Contributions to the Basic Problems of Complexometry—VII: Estimation of Copper and Iron: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (31 *May* 1961).

Spectrophotometric Determination of Rhodium after Oxidation with Hypobromite: FRANCESCO PANTANI. (1 *June* 1961).

Photometric Titrations—IV: The Consecutive Titration of Calcium and Magnesium: H. FLASCHKA and J. GANCHOFF. (2 *June* 1961).

A Universal Automatic Recording Titrator: ANTONY ANTON and PAUL W. MULLEN. (6 *June* 1961).

Rate of Hydrolysis of Thiolacetic Acid in Basic Solutions: M. CEFOLA, SIMON PETER, P. S. GENTILE and A. V. CELIANO. (6 *June* 1961).

A Note on the Use of Vanadium^{V}-sulfosalicylic Acid Complex as a Redox Indicator: V. PANDU RANGA RAO and D. SATYANARAYANA. (6 *June* 1961).

A New Sensitive and Specific Test for Vanadium^{V} with Sulphosalicylic acid as Reagent: V. PANDU RANGA RAO and D. SATYANARAYANA. (6 *June* 1961).

Titrimetric Determination of Orthophosphate with Uranium^{VI}: Use of Resacetophenone-oxime as an External Indicator: C. RAMA RAO. (6 *June* 1961).

Contributions to the Basic Problems of Complexometry—VIII: The Determination and Masking of Aluminium: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (9 *June* 1961).

Some Theoretical and Practical Problems in the Use of Organic Reagents in Chemical Analysis—I: Effect of Donor π Bonds on the Stability of Chelate Complexes Containing Sulphur: K. BURGER. (12 *June* 1961).

A Polarographic Study of Dissolved Oxygen—I: V. S. GRIFFITHS and M. I. JACKSON. (12 *June* 1961).

A Critical Examination of Methods Used for the Determination of "Available Oxygen" in Higher Metal Oxides: D. A. PANTONY and Mrs. A. SIDDIQUI. (13 *June* 1961).

Thermogravimetric Analysis of Potassium Hydrogen Phthalate: A. E. NEWKIRK and RENETTE LAWARE. (13 *June* 1961).

Chelatometric Determination of Cyanide, Thiocyanate and Chloride in Presence of One Another: ARTHUR DE SOUSA. (14 *June* 1961).

Applications de la Chélatométrie—XV: Dosage Volumétrique du 6-Pureinthiol: CLAUDE HENNART. (16 *June* 1961).

Semimicro Determination of Strontium and Calcium in Mixtures: C. HEITNER-WIRGUIN and A. ALBU. (20 *June* 1961).

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FIG. 1. A. STEYERMARK (U.S.A.), Chairman of the Committee for the **International Symposium on Microchemical Techniques,** 13–18 August, 1961, organised by the Metropolitan Microchemical Society under the sponsorship of I.U.P.A.C., welcomes participants at the first Plenary Session.

FIG. 2. Speakers at one of the Technical Sessions of the Symposium (left to right): A. M. TROZZOLO (U.S.A.), A. LACOURT (Belgium), H. WALDMANN (Switzerland), M. BRANDSTÄTTER-KUHNERT (Austria), A. KOFLER (Austria) and W. C. MCCRONE (U.S.A.).

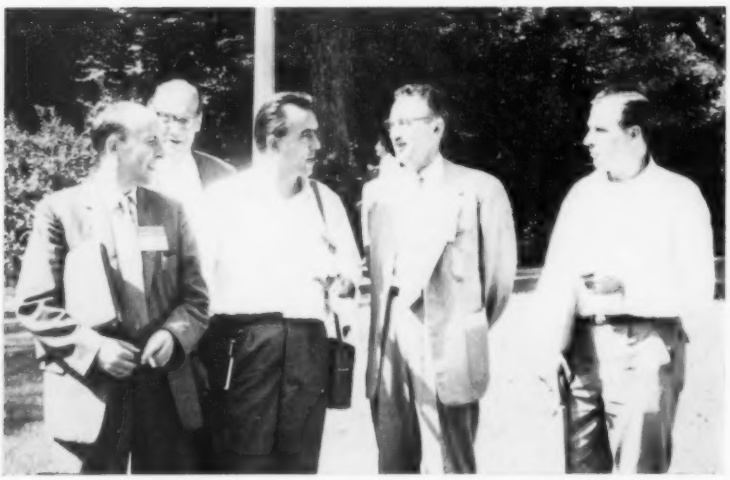

FIG. 3. A group on the campus of Pennsylvania State University, U.S.A., where the Symposium was held (left to right): G. INGRAM (U.K.), H. MALISSA (Austria), W. SCHÖNIGER (Switzerland), C. L. OGG (U.S.A.) and S. HÖLZL (Austria).

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DIE BESTIMMUNG KLEINER FLUORMENGEN—I

EINE KRITISCHE ÜBERSICHT

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Zusammenfassung—Eine kritische Studie, in welcher festgestellt wird, daß bei den verschiedenen Typen der Fluorbestimmung sowohl mit als auch ohne Trennung im Prinzip dieselben Komponenten stören. Eine Gleichung, welche die Verhältnisse bei der destillativen Fluorabtrennung wiedergibt, wurde abgeleitet und mit veröffentlichten, experimentellen Resultaten verglichen. Die Literaturangaben sind nur selten älter als aus dem Jahre 1955.

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DIE Bedeutung der Fluorbestimmung ist vielseitig. In Trink-und Mineralwässern und weiter in der Luft, hauptsächlich von Aluminium- bzw. Fluorwerken, ist es aus gesundheitlichen Gründen notwendig, den Fluorgehalt zu verfolgen. Da die Grenzen des hygienisch unbedenklichen Fluorverbrauches manchmal sehr eng angegeben werden (1,3–1,5 mg pro Tag),[1] müssen die Bestimmungen genau durchgeführt werden. In der Hydrogeologie beurteilt man nach der Fluoridkonzentration die Genese mancher Thermalwässer und in der Archäologie das Alter der Knochen nach der Relation ihres Fluorgehaltes zu ihrem Phosphatgehalt. In der Industrie, organischen Chemie und Physiologie ist es z.B. notwendig, Fluorverunreinigungen im Aluminium, das unter Zusatz von Kryolith hergestellt wird, oder Fluor in einer Reihe bedeutender organischer Verbindungen (Freone, Teflon, "Nerven"-Gifte, usw.) zu bestimmen.

In natürlichen Materialien und hauptsächlich in Mineralwässern kann das Fluor in einigen Formen vorkommen, nämlich als Fluorid, Fluoaluminat, Fluoferrat, Fluosilikat, Fluoborat usw. Deshalb muß man vor allem seinen Gesamtgehalt bestimmen, welcher meistens ungenau als "Fluoridgehalt" bezeichnet wird. Diese Arbeit gibt eine kritische Übersicht der diesbezüglichen analytischen Methoden. In der Zukunft wird es jedoch notwendig sein, auch einzelne Existenzformen des Fluors zu bestimmen, denn es erscheint von vornherein nicht ausgeschlossen, daß der physiologische Einfluß von Fluorid ein anderer ist als der von stabilen Fluorsystemen.

Die Bestimmung kleiner Fluormengen wird gegenwärtig meistens spektralphotometrisch und photometrisch durchgeführt. Zu diesem Zweck nützt man vor allem die entfärbende Wirkung der Fluoride auf Farblacke und -chelate von mehrwertigen Kationen mit organischen Farbstoffen aus. Die Entfärbung anorganischer Komplexe ist weniger günstig. Immer wieder studiert man die Lacke von Alizarin S, in diesem Zusammenhang gewöhnlich nur als Alizarin bezeichnet,[2–5] von Purpurin-Sulfat[6] mit Zirkonium und von Alizarin S mit Thorium;[7,8] neuerdings finden auch folgende Kombinationen Anwendung: Chromazurol S,[9] Amarath,[10] Thoron[11] bzw. Phenylfluoron,[13] Neothorin[12] mit Thorium; Eriochromcyanin R,[14–19] Brenzkatechinviolett,[20] SPADNS,[21] weniger gebräuchliche Farbstoffe[22,23] und in letzter Zeit Xylenolorange[109]

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mit Zirkonium; Aluminon,[24] Haematoxylin,[25] Chromazurol S[26,27] bzw. Eriochromcyanin R[27,28] mit Aluminium; Salicylsäure,[29] Antipyrin[30] und eine Reihe anderer Reagentien[31] mit Eisen(III); Chromotrosäure,[32] Phenylfluoron[33] und Ascorbinsäure[34] mit Titan und schließlich Chromazurol S mit Beryllium.[35]

Weiterhin werden auch schwerlösliche Verbindungen herangezogen, die bei der Reaktion mit Fluorid eine photometrierbare Komponente freigeben, z.B. Lanthan-[36] und Thoriumchloranilat[37] oder Zirkonium-4-Dimethylaminoazobenzol-4-arsenat.[38] Man benutzt auch den Inhibitoreinfluß der Fluoride auf die Phosphatase und photometriert das freigewordene Phosphat[39,40] bzw. die katalytische Redoxreaktion zwischen Ce(III) und Ce(IV) Ionen.[41] Die einzige bekannte Farbreaktion mit Fluorid ermöglicht eine Lösung von Cer(III)-3-aminomethylalizarin-N,N-Diacetat, welche für qualitative[42] und mit ungleichem Erfolg für quantitative[43,110,119] Zwecke benutzen kann, siehe auch.[110] Fluorometrische Fluorbestimmungen lassen sich mit den Aluminiumchelaten von Oxychinolin oder Morin,[44] Eriochromarot B bzw. Superchrom Garnet Y[45] ausführen. Niedrige Fluorgehalte werden auch herkömmlich volumetrisch bestimmt, und zwar mit visueller,[46,47] photometrischer,[48,49] fluorometrischer,[50] turbidimetrischer,[51] potentrimetrischer,[52] amperometrischer,[53–55] konduktometrischer,[56,57] Hochfrequenz-[58,59] bzw. radiometrischer[60] Indikation. Neulich gebrauchte man eine coulometrische[111] und dead-stop[112] Titration.

Man titriert in der Regel mit Lösungen derselben Kationen, welche bei den photometrischen Bestimmungen gebraucht werden. Bei visueller Endpunktsanzeige verwendet man auch meistens dieselben Farbstoffe.

Zu polarographischen Bestimmungen nützt man polarographisch aktive Chelate oder Komplexe mit verschiedenen der erwähnten Kationen aus, z.B. mit Aluminium[61] oder Eisen,[62] und inaktive Chelate, z.B. mit Thorium, welche aktive Stoffe freigeben.[63] Man verwendete auch die innere Elektrolyse mit einer Zirkonelektrode.[64]

Die Empfindlichkeit der angewendeten chemischen Fluorbestimmungen ist nicht nur von den Eigenschaften der mit dem Fluorion reagierenden Komplexe (von ihrer Farbintensität usw.) im Zusammenhang mit einer guten Indikation des Reaktionsablaufs abhängig, sondern auch von den stöchiometrischen Verhältnissen in den entstehenden Verbindungen. In diesen kann das Verhältnis Fluor zu Kation sehr verschieden sein; in der Literatur wird 6, 4, 2 bis 1:1 angegeben. Es entstehen z.B. TiF_6^{2-}, ThF_4,[55] $ZrOF_2$,[4] FeF^{2+} [30] und $TiOF^+$.[32]

Bei den chemischen Fluorbestimmungen, die sich eigentlich nur auf einige sehr verschiedenartig verfolgte Grundreaktionen stützen, werden die Resultate stets mehr oder weniger durch Anionen erhöht, die ähnliche Eigenschaften wie das Fluorion besitzen. Es sind dies hauptsächlich Phosphate (welche praktisch bei allen Bestimmungen stören), Sulfate (welche bei Gebrauch von Zirkon, Thorium, Lanthan, Cer und manchmal auch Eisen und Titan stören), bzw. auch Arsenate, Borate, Chloride usw. Höhere Resultate werden auch durch Oxydationsmittel, z.B. Chlor, verursacht, welche die benutzten organischen Stoffe zersetzen. Negative Fehler können auftreten, indem das Fluorion durch Aluminium-, Eisen(III) Ionen bzw. Kieselsäure getarnt wird, oder z.B. Eisen(III)- bzw. Manganionen mit dem angewandten Farbstoff unerwünschte Chelate bilden.

Bei dem Gebrauch von Cer(III)-aminomethylalisarin-N,N-Diacetat wird ein Fehler von 10% z.B. bei einem 650maligem Sulfat und 0,3maligem Aluminium-Ionen Überschuß verursacht.[110] Beim Gebrauch von Zr-Xylenolorange beträgt nach

vorläufigen Angaben[109] der Fehler eines 5maligen Aluminium-Ionen Überschusses 0% und eines 1000maligen Sulfat Überschusses 12%; bei entsprechenderen Bedingungen, welche später veröffentlicht werden, stört auch ein 3–5 Tausendmaliger Überschuß von Sulfaten nicht.

Wenn man in der Methode,[42] in welcher Belcher und Mitarbeiter das erste mal einen Farbstoff mit einer di(carboxymethyl)-amino-methyl Gruppe zur Bestimmung von Fluor ausnützten, anstatt die Cer(III)-Ione diejenigen von Zirkonium gebrauchen möchte, würde man mit größter Wahrscheinlichkeit ähnliche Resultate wie mit Xylenolorange bekommen (log der Stabilitätskonstanten von CeF^{2+} und ZrF^{3+} sind 3,11 und 8,71[75]). Da die Konstante von CeF^{2+} markant kleiner als die von AlF^{2+} (6,13) und FeF^{2+} (5,17) und größer als die von CaF^{+} (0,51) und MgF^{+} (1,30) ist und da bei der Methode[42,110] Sulfate und Phosphate nicht beträcht lich stören, könnte man sie mit Vorteil zur Bestimmung des freien bzw. wenig stabil gebundenen Fluors in vielen Wässern gebrauchen. Den Einfluß von Ca-Ionen, welcher sich nach experimentellen Angaben[110] schon von einem 10maligem Überschuß anoffenbart, wird man mittels Korrektionsnomogramme eliminieren müssen. Das auf diese Weise bestimmte Fluor könnte dem biologisch aktiven Fluor entsprechen—man kann sich nämlich vorstellen, daß z.B. das Fluor, welches die Atmung der Pflanzen vermindert,[120] das die Enolase aktivierende Magnesium tarnt, welches die Respiration erhöht.

Aus höher angeführten Gründen ist es deshalb sehr vorteilhaft, in manchen Materialien, besonders in Aluminium, den Fluorgehalt spektrographisch auf Grund der Molekularbande von CaF und SrF zu bestimmen.[65,66] im metallischen Zirkonium wird er in Heliumatmosphäre mittels der Atomlinien von Fluor oder besser des Molekülbandsystems von Zirkoniumfluorid[113] bestimmt. Zur aktivierungsanalytischen Bestimmung von Fluor wurde die mit thermischen Neutronen induzierte Aktivität des Isotops ^{20}F (Halbwertszeit- 11 sec.)[67] oder die durch schnelle Neutronen hervorgerufene Aktivität des Isotops ^{16}N (7,6 sec.)[68] benutzt. Die hofnungsvollste Reaktion $^{19}F(n, 2n)^{18}F$ (112 min., Empfindlichkeit 0,1 μg F)[114] wird sicher auch bald analytisch ausgenützt werden. Vor kurzem nützte man auch die nukleare magnetische Resonanz[115] aus.

Da bei der Bestimmung des Fluor-Gesamtgehaltes eine Anzahl von Komponenten stört, versuchte man immer dessen Abtrennung. Am gebräuchlichsten ist hierzu das schon klassische Destillationsverfahren (s. Offermann 1890). Ihm wird deshalb hier besondere Aufmerksamkeit gewidment.

In welcher Form das Fluor destilliert, ist z.B. in den Arbeiten [69,70] beschrieben.

Bei dem überwiegenden Destillationstyp[71] kann man das Fluor von einer etwa äquimolaren Menge von Zirkonium überhaupt nicht trennen.[72] Aus dem Milieu einer konzentrierten Aluminium-Lösung ist die Geschwindigkeit der Fluorabtrennung eine im Prinzip logarithmische Funktion der Zeit[70] und wird bei einem annähernd hundertfachen Aluminium-Überschuß praktisch Null. Weiter fanden Rennert und Mitarbeiter[73] bei der Destillation aus 1 g Pflanzenmaterial 30 ppm F und aus 10 g derselben Probe 7 ppm F; z.B. in 1 und 5 g desselben Grases wurden 44 und 35 ppm F gefunden.[74] Ein ähnlicher Effekt, welcher bei der Bestimmung von Fluor ohne Abtrennung von Aluminium beobachtet wurde, wird später angeführt.

Die Ursache der erwähnten Schwierigkeiten liegt in der Abhängigkeit des Partialdruckes des abzudestillierenden Fluorwasserstoffes über der Lösung von seiner

Konzentration in der Lösung, welche ihrerseits eine Funktion der Stabilitätskonstanten der entsprechenden Fluorsysteme und der Konzentration aller Kationen, Silikate und Borate in der Lösung ist. Da die Stabilität der Fluorsysteme, insbesondere von Zirkonium und auch von Aluminium, außerordentlich hoch ist,[75] sind die Fehler, welche durch die Anwesenheit dieser Elemente im zu analysierenden Material verursacht werden, sehr markant. Die Resultate der Arbeiten[73,74] rühren davon her, daß bei größeren Einwaagen die Komponenten, welche Fluorsysteme bilden, infolge ihrer erhöhten Konzentration in der Destillationslösung das Fluor stärker binden und seinen abdestillierbaren Anteil herabsetzen.

Quantitativ kann obige Erklärung für die Unvollkommenheiten der destillativen Fluorabtrennung durch die im weiteren Text abgeleitete Gleichung wiedergegeben werden:

$$s_F = S_F(1 - e^{-kAt}) \tag{1}$$

Hierin bedeuten S_F die ursprünglich vorhandene und s_F die zur Zeit t abdestillierte Fluormenge.

Die Gleichung folgt aus der allgemeinen Geschwindigkeitsgleichung 1. Ordnung für die Destillation von Flußsäure

$$-\frac{d_{CHF}}{dt} = k \,.\, C_{HF} \tag{2}$$

wobei sich C_{HF} mit C_{F^-} und C_{MF} im Gleichgewicht befindet. MF ist die einfachste Form eines Metallion-Fluorion-Systems in der Lösung, das die destillative Fluorabtrennung stört.

$$C_{HF} = K_{HF} \,.\, C_{H^+} \,.\, C_{F^-} = K_{HF} \,.\, C_{H^+} \,.\, K_{MF}{}^{-1} \,.\, C_{M^+}{}^{-1} \,.\, C_{MF} \tag{3}$$

K_{HF} und K_{MF} sind die Stabilitätskonstanten der Flußsäure bzw. des Fluorion-Metallion-Systems. Im allgemeinen Fall, bei dem in der Lösung m MF bis MF_n Systeme vorliegen, lautet der Ausdruck

$$C_{HF} = K_{HF} \,.\, C_{H^+} \sum_m \left(\sum_{n=1}^{n} K_{MF_n}^{-1} \,.\, C_{MF_{n-1}}^{-1} \,.\, C_{MF_n} \right)_m \tag{3a}$$

Bei in der Wirklichkeit vorkommenden hohen Konzentrationen der Säure und anderer Komponenten der Lösung, aus welcher destilliert wird, muß man auch deren Aktivitätskoefizienten in Betracht nehmen. Es soll jedoch nur ein einziges System MF betrachtet werden. Für den praktisch wichtigen Fall $C_{M^+} \gg C_{MF}$ läßtsich schreiben

$$C_{HF} = B \,.\, C_{MF} \quad \text{wobei} \quad B = K_{HF} \,.\, C_{H^+} \,.\, K_{MF}{}^{-1} \,.\, C_{M^+}{}^{-1} \tag{4}$$

Da im betrachteten Beispiel das Fluor als Fluorwasserstoff abdestilliert wird, gilt in Gleichung (2) die Identität

$$-\frac{dC_{HF}}{dt} \equiv -\frac{dC_F}{dt} \tag{5}$$

C_F ist die Fluor-Totalkonzentration in Lösung.

$$C_F = C_{HF} + C_{MF} + C_{F^-} = A^{-1} \,.\, C_{HF}$$

wobei $$A^{-1} = 1 + B^{-1} + K_{HF}^{-1} \,.\, C_{H^+}^{-1} \text{ und } A = \frac{K_{HF} \,.\, C_{H^+}}{K_{HF} \cdot C_{H^+} + K_{MF} \cdot C_{M^+} + 1} \tag{6}$$

Wenn $K_{MF} \cdot C_{M^+} \geqslant 1 + K_{HF} \cdot C_{H^+}$, dann $A = K_{HF} \cdot C_{H^+} \cdot K_{MF}^{-1} \cdot C_{M^+}^{-1} = B$ und wenn $K_{MF} \cdot C_{M^+} + 1 \ll K_{HF} \cdot C_{H^+}$, dann $A = 1$.
Somit geht Gleichung (2) in den Ausdruck

$$-\frac{dC_F}{dt} = k \cdot A \cdot C_F \tag{7}$$

über. Integration in den Grenzen $t = 0$ bis t liefert

$$\frac{(C_F)_t}{(C_F)_0} = e^{-kAt} \tag{7a}$$

$(C_F)_t$ ist die zur Zeit t, $(C_F)_0$ die zur Zeit 0 vorhandene Fluor-Totalkonzentration in der Lösung. Der Konzentrationsverlust durch Destillation beträgt $(C_F)_0 - (C_F)_t = \frac{s_F}{v}$, wo v das Lösungsvolumen bedeutet. Mit dem entsprechenden Ausdruck $(C_F)_0 = \frac{S_F}{v}$ wird aus Gleichung (7a) schließlich die Gleichung (1) erhalten:

$$s_F = S_F(1 - e^{-kAt})$$

wobei A den Wert von 1 bis $B \ll 1$ hat.

Die Größe k enthält wahrscheinlich nur noch die Abhängigkeit α der Fluorwasserstoffkonzentration C_{HF} in und c_{HF} über der Lösung und experimentelle Parameter, d.h. Werte, welche von der Form der Destillationsapparatur, der Destillationsgeschwindigkeit usw. abhängen. Sie werden in der Größe η zusammengefaßt, die man als quantitatives Maß für die Effektivität der einzelenn veröffentlichten, bis jetzt aber objektiv nicht vergleichbaren Varianten der destillativen Fluorabtrennung benutzen könnte. Im allgemeinen Falle kann die Größe k auch die Geschwindigkeitskonstante k_{MF} des Zerfalles von MF in M^+ und F^- enthalten. Also $k = M\alpha^{-1}k_{MF}$.

Eine vorläufige halbquantitative Bestätigung der angeführten Interpretationen kann in der in letzter Zeit veröffentlichten Arbeit[108] gesehen werden, welche den Destillationsverlauf von Fluor aus einer sauren Lösung von Aluminiumfluorid verfolgt. Aus der Abbildung, in welcher auf der Abszisseder Logarithmus des nicht überdestillierten Fluorgehaltes log $(S_F - s_F)$ und auf der Ordinate die Zeit t aufgetragen wird, ist nämlich ersichtlich, daß der Verlauf des log $(S_F - s_F)$ zuerst durch eine Gerade der Neigung—1,3 wiedergegeben wird, welche nach einer bestimmten Zeit in eine Gerade der Neigung —0,78 und endlich —0,42 übergeht. Nach der oben entwickelten Vorstellung sollten die einzelnen Destillationsgeschwindigkeiten, welche durch ihre Richtungsfaktoren charakterisiert sind, die man als Destillationsgeschwindigkeits-Konstanten bezeichnen könnte, dem nacheinander verlaufenden Zerfall der zunehmend stabileren Systeme AlF_3, AlF_2^+ und AlF^{2+} entsprechen. Die Abhängigkeit, welche durch Vergleich der einzelnen Richtungsfaktoren $K_n = \Delta \log (S_F - s_F)/\Delta t$ mit den Logarithmen der Stabilitätskonstanten der entsprechenden Fluoaluminate (siehe Fig. 1) erhalten wurde, befindet sich nicht im Widerspruch zu den Gleichungen (1) und (2), indem s_F bzw. $-dc_{HF}/dt$ den Stabilitätskonstanten der in der Lösung anwesenden Fluorsysteme indirekt proportional sind. Infolge der Dissoziation der Fluoaluminate, welche bei den weniger stabilen Systemen selbstverständlich größer als bei den festeren ist, entstehen die Knicke der Destillationskurve erst nach dem Überdestillieren von 60 und 82% Fluor. Wenn aber in der Arbeit[108] aus einer Lösung

mit Zugabe von Phosphorsäure destilliert wird, welche die Destillation von Fluor im allgemeinen verlangsamt (Entstehung festerer ternärer Aluminium-Fluor-Phosphat-Systeme?), zeigen sich die Knicke in der Destillationskurve nach dem Überdestillieren von 45 und 66% Fluor. Der letzte Knick deutet ziemlich genau auf die Existenz eines Systems mit dem Verhältnis Al:F = 1:1 hin, aus welchem das Fluor infolge geringer Dissoziation nur noch sehr langsam destilliert.

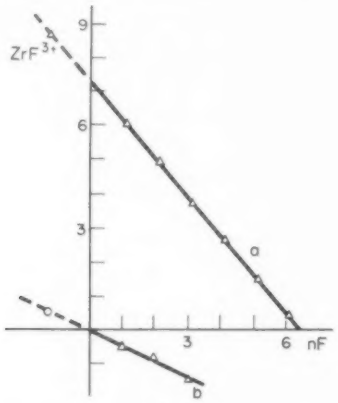

ABB. 1

(*a*) Logarithmen der Stabilitätskonstanten der Fluosysteme $AlF_n^{(3-n)+}$ bei 25°, übernommen aus[75].
(*b*) Werte der Richtungsfaktoren $K_n = \Delta \log (S_F - s_F)/\Delta t$ der einzelnen Abschnitte der Destillationskurve von AlF_3 bei 125°C, übernommen aus[108].
Zu den Werten auf dem gestrichelten Teil der Kurven siehe die Erläuterungen im Text.

Wenn man die Geraden *a* und *b* in Abb. 1 so verlängert, daß man auf *a* ohne Rücksicht auf die Anzahl nF den Logarithmus der Stabilitätskonstante von ZrF^{3+} eintragen kann, so lassen sich auf dem verlängerten Teil der Gerade *b* die Verhältnisse erfassen, welche bei Destillation aus einer ZrF^{3+}-Lösung unter den Bedingungen der Arbeit[108] gelten. Wenn nämlich die Fluordestillation bei sonst konstanten Bedingungen nur um so schwieriger verläuft, je fester Fluor in einem beliebigen System gebunden ist, kann man nicht nur erwarten, daß z.B. die Destillation aus einer Lösung von ZrF_3^+ ($\log K_3 = 5{,}74$)[75] ähnlich verläuft wie aus einer Lösung von AlF^{2+} ($\log K_1 = 6{,}13$), sondern man kann aus dem Verlauf der Destillationsgeschwindigkeits-Konstanten einiger Fluoaluminate in Abhängigkeit von deren Stabilitätskonstanten auch die Werte der Destillationsgeschwindigkeit anderer Systeme abschätzen, sofern deren Stabilitätskonstanten bekannt sind. Aus Abb. 1 geht auf Grund dieser Voraussetzung hervor, daß aus der ZrF^{3+}-Lösung kein Fluor destillieren wird, was mit der Erfahrung übereinstimmt.

Ähnliche Werte könnte man auf Grund desselben Prinzips bekommen, indem man direkt die Kurven der Stabilitätskonstanten und der Destillationsgeschwindigkeits-Konstanten von Zirkonium ableiten würde.

Durch Auswertung einer experimentell und theoretisch gründlicher verfolgten Formulierung der angeführten Gleichung wird man die Grenzen für die Verwendbarkeit der Destillationstrennung von Fluor erfassen und die Fehler dieses "klassischen" Verfahrens unter weniger günstigen Bedingungen bzw. bei früher durchgeführten Analysen abschätzen können.

Besonders wichtig ist es, in der Destillationslösung die höchstzulässigen Konzentrationen an Kalzium und Magnesium festlegen zu können, deren Oxyde organischen und biologischen Analysenproben zur Unterdrückung von Fluorverlusten bei der Veraschung beigemischt werden. Zu hohe Erdalkalizusätze verfälschen die Ergebnisse wahrscheinlich nicht nur absolut, sonder auch relativ. Im Extremfall könnte der nicht überdestillierte Fluor-Anteil im Sinne der Versuche[73,74] bei einem hohen Fluor-Gehalt 0% und bei einem niedrigen Fluor-Gehalt 100% betragen.

Man kann erwarten, daß sich die Faktoren, welche den Verlauf der destillativen Fluorabtrennung beeinflussen, wenigstens im Prinzip auch bei den anderen analytischen Destillationsverfahren durchsetzen werden. Die Ausarbeitung einer Destillationstheorie von Fluor könnte vielleicht einen Anlaß zum Aufbau einer allgemeinen Theorie der analytischen Destillationsverfahren geben.

Die besseren Fluorabtrennungen, welche durch eine Erhöhung der Destillationstemperatur über 135°C erzielt werden, sind von störenden flüchtigen Bestandteilen begleitet. Bei der Destillation aus Perchlorsäurelösungen wird die Säure teilweise zu Chlor reduziert, welches auch schon bei niedrigeren Temperaturen, z.B. durch den Einfluß der Chloride, gebildet werden kann, sofern diese aus der analysierten Lösung nicht entfernt wurden.[1] Bei derDestillation aus Schwefel- bzw. Phosphorsäurelösungen werden demgegenüber nicht vernachlässigbare Mengen von deren Dämpfen abgegeben, weshalb man z.B. ein zweites Mal bei niedrigerer Temperatur destilliert[76] oder das überdestillierte Sulfat fällt.[77]

Da auch die neueren Modifikationen der Fluordestillation[19,73,74,77] nur vorwiegend der organischen Mikroanalyse Verbesserungen bieten, widmet man in der letzten Zeit der Stromdestillation, meist Pyrohydrolyse genannt,[78–83] erhöhte Aufmerksamkeit.

Die Fluorabtrennung wird hier unter Durchleiten von Wasserdampf durch die Probe bei Temperaturen von 600–1000°C in Anwesenheit von Katalysatoren erzielt. Auf diese Art kann man Fluor auch von Zirkonium trennen.[78] Die zur Bestimmung von mg-Mengen günstige pyrohydrolytische Abtrennung kann aber nur schwierig bei der Isolierung von μg-Mengen benutzt werden, welche z.B. in den üblichen analytisch verarbeiteten Volumina von Naturwässern vorhanden sind, da in den gebräuchlichen Apparaturen leicht Verluste des freigesetzten Fluors entstehen. —Bei der sog. Technik der Schönigerflaschen,[84] bei welcher die zu analysierenden Proben in einer Sauerstoff-Wasserstoff-Flamme verbrannt werden,[18,43,85] entstehen noch bei einem Gehalt von 10 mg F Fluorverluste von 10%.[43] Bei den Hochtemperaturtrennungen destillieren schließlich auch einige die Fluordestillation störenden Anionenkomponenten mit über.

Obwohl man durch Pyrohydrolyse auch Fluor von Zirkonium trennen kann, kann man voraussetzen, daß für alle Destillationsverfahren, ebenso wie für das Veraschen oder das alkalische Schmelzen von fluorhaltigen Proben, ähnliche Gleichungen gelten werden, wie die oben angeführten. An die weniger bekannte Existenz von Chelaten bzw. Komplexen bei hohen Temperaturen sei hier nur erinnert. Z.B. ist es üblich, Kalzium bei der flammenphotometrischen Bestimmung der Alkalien mit Hilfe von Phosphat zu tarnen. Auch die schon angeführte spektrographische Bestimmung von Fluor ist nur durch die Stabilität von CaF und SrF oder eines Fluor-Zirconium-Systems im Milieu des elektrischen Bogens möglich.

Es ist zu erwarten, daß die bis jetzt fast völlig vernachlässigte Chemie der Chelate

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und Komplexe unter extremen Bedingungen von der Fluorchemie neue Impulse erhalten wird.

Die bei den Bestimmungen von mg-Fluormengen störenden Kationen wurden mit Kationenaustauschern im H-[86–91] bzw. Na-Zyklus[92] abgetrennt. Von 1 ppm Fluor kann man mindestens 20fache Überschüsse aller Kationen mit Ausnahme von Zirkonium und Aluminium trennen.[4] Phosphate[93–95] wurden, ebenso wie die EDTA-Komplexe bildenden Kationen[96] von Anionenaustauschern sorbiert. Eine Abtrennung von hohen Sulfatüberschüssen glückte aber weder auf diesem Wege,[97] noch mit einem Kationenaustauscher im Ba-Zyklus.[98] Verschiedenen Autoren gelang es, das Fluor mit einem Kationenaustauscher in Th-Zyklus[99] bzw. mit einem synthetischen Zirkonylsilikat[100] zu isolieren. Die Resultate schwankten jedoch, und die Sorption der Sulfate wurde überhaupt nicht verfolgt. Die Verluste durch Adsorption von Fluor an Glas wurden untersucht[101] und auf Grund dieser eine Isotopenverdünnungsmethode unter Anwendung des Radioisotops F^{18} ausgearbeitet.[102]

Die Isolierung des Fluors durch Extraktion gelang nur aus relativ konzentrierten Lösungen.[103]

Die Mängel der einzelnen Abtrennungsverfahren sind vielleicht am besten aus einer kürzlich veröffentlichten Arbeit[104] ersichtlich: eine Fluormenge von über 2 mg wird erstens pyrohydrolytisch von den Kationen, danach mit einem Anionenaustauscher von den Nitraten und endlich mit einer indirekten Extraktionsbestimmung von den Sulfaten getrennt. Das der Lösung beigemischte Hafnium, welches radioaktives[181] Hf enthält, wird mit Trioktylphosphin-Oxyd in Hexan extrahiert. Auf Grund der radiometrisch bestimmten Verteilung des Hafniums zwischen den beiden Flüssigkeitsphasen wird dann die Menge des extraktionshemmenden Fluorids durch Vergleich mit einer Standardkurve ermittelt.

Bei der Fluorabtrennung stören also dieselben Komponenten wie bei Fluorbestimmungen ohne vorherige Trennung: Die Komponenten, welche stabile Fluorsysteme bilden, vermindern oder verlangsamen wenigstens die Isolierung bei der Destillation, beim Ionenaustausch und bei der Extraktion. Anionen mit ähnlichen systembildenden Eigenschaften wie Fluoride, hauptsächlich Sulfate, kann man insbesondere durch Ionenaustausch bzw. Pyrohydrolyse nur schwierig trennen. Unter den extremen Bedingungen der Hochtemperaturtrennungen, von denen die Pyrohydrolyse als bestes Verfahren anzusehen ist, findet zwar eine vollständige Freisetzung des Fluors statt, aber es entstehen besonders bei μg-Bestimmungen in der Apparatur relativ hohe Fluorverluste.

Die Trennungsverfahren sind ferner auch deshalb ungünstig, weil sie größere Apparaturansprüche stellen. Deshalb suchte man immer nach Methoden, welche durch Verminderung des größten Störeffektes auch ohne eine Trennung genügend richtige Resultate, wenigstens in einem bestimmten Material, liefern. So kann man niedrige Sulfatüberschüsse bei manchen Verfahren durch genaue Korrekturen mit Hilfe von Nomogrammen berücksichtigen.[14] Bei anderen Methoden vermindert man den Einfluß der Sulfate im Gegenteil durch eine größere Sulfatzugabe zum Fluor Reagens,[2] wobei man die relativ geringe Entfärbungswirkung hoher Sulfatkonzentrationen ausnützt. Verschiedene Autoren vermindern den Sulfat-[46] bzw. Phosphateinfluß[91] durch Zugabe von Kalzium zur Lösung, und andere beseitigen die Sulfate als Bariumsulfat,[15,105] ohne experimentelle Ergebnisse anzugeben. Da man jedoch bei manchen Fluor-Mikrobestimmungen mit dem erwähnten Niederschlag das Bariumfluorid mitreißt,[106] ist es notwendig, die angeführten Verfahren zu überprüfen.

Durch Erhöhung der Farbstoffkonzentration wird die Störwirkung der Phosphate verringert, z.B. bei der Zirkonium-Alizarin-Methode um eine Größenordnung.[3] Dies hängt mit einer Zurückdrüngung der Dissoziation des benutzten Chelats zusammen. Ähnlich wirkt sich auch die Verminderung des pH-Wertes der Lösung aus,[15] wobei auch die Fluoaluminate rascher zersetzt werden.[15]

Die Fluorbestimmung ist bei gleichem relativen Aluminiumüberschuß fehlerhafter bei einer höheren Fluorkonzentration. So werden unter sonst gleichen Bedingungen in 100 ml der Lösungen von 50 μg F neben 50 μg Al noch 44 μg F, von 100 μg F neben 100 μg Al jedoch nur noch 83 μg F gefunden.[2]

Das hängt in ähnlicher Weise, wie bei der Destillation angeführt wurde, mit der größeren Dissoziation der Fluosysteme bei niedrigeren Konzetrationen zusammen. Analog bildet sich bei niedrigen Boratkonzentrationen kein Fluoborat.[107]

Infolge der prinzipiellen und praktischen Unvollkommenheit der "universellen" Trennungsverfahren hat es der Autor für notwendig gehalten, aus den Teilkenntnissen über die Eliminierung der einzelnen Störwirkungen Regeln für die Erforschung praktisch anwendbarer Bestimmungen des Fluor-Gesamtgehaltes ohne Abtrennung zusammenzustellen. Ausführlich werden diese Regeln, welche schon in der Arbeit[109] angedeutet wurden, später veröffentlicht.

Großere Übersichten der älteren Bestimmungen von Fluor sind in den Arbeiten 116–118 enthalten.

Notiz. Eine theoretische und experimentale Studie über die Destillation von Fluor aus komplexbildendendem Milieu wird vorbereitet. Praktisch wird die Destillation hauptsächlich zur Bestimmung von Fluor in Zirkonium-Präparaten ausgenützt. Im Destillationskolben wird Zirkonium mit einem geeignetem Tarnmittel gebunden, dessen einfachste sonts aber weniger geeignete[76,77] Form schon die Schwefel- oder Phosphorsäure ist. Das freigewordene Fluor wird danach aus genügent saurer Lösung abdestilliert und bestimmt. Ähnlicherweise könnte man fluorfreies Zirkonium, Aluminium, usw. zubereiten.

Zu großem Dank bin ich Herrn W. Leonhardt, Dresden verpflichtet, der an der endgültigen Fassung dieser Arbeit beteiligt war.

Summary—In a critical study it is established that in the different types of fluorine determination, with or without prior separation, the same components interfere. An equation is derived which permits the determination of the quantity of fluorine separated during distillation. Values obtained are compared with published results which have been obtained experimentally. Literature references are mainly to material published after 1955.

Résumé—Dans une étude critique, l'auteur établit que dans différents types de dosage du fluor, avec ou sans séparation préalable, les mêmes composés gênent. Une équation en est déduite et permet le dosage de la quantité de fluor séparée pendant la distillation. Les valeurs, obtenues sont comparées avec les résultats publiés obtenus expérimentalement. Les références de la littérature sont principalement des articles publiés après 1955.

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THE DETERMINATION OF SUB-MICRO QUANTITIES OF THIOL COMPOUNDS

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Summary—A method based on a procedure devised by Saville[1] has been developed for the determination of thiol compounds in alcoholic and hexane solutions at concentrations of 0·0005 to 0·005*M*. The thiol compound is oxidised by bromine water to a sulphonyl bromide which is converted to cyanogen bromide and determined colorimetrically by the method of Aldridge.[2]

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INTRODUCTION

A PROCEDURE for determining low concentrations of long chain aliphatic thiols has been developed in order to follow small concentration changes of these compounds when used as dropwise condensation promotors in hexane solution.

Brockhuysen[3] has described a photometric method for this determination, based upon the red colour given by thiols in an alcoholic medium using *N*-ethylmaleimide. Attempts to repeat the work of Brockhuysen were not successful; the optical densities of the coloured solutions were found to reach maximum values very quickly and to remain constant for only a very short time.

Kunkel, Buckley and Gorin[4] have described a method for determining thiols in hydrocarbon solution, in which the thiol is added to a solution of silver dithizonate in carbon tetrachloride. The liberated dithizone is then determined spectrophotometrically. Attempts were made to use this procedure for a number of thiols. Excellent results were obtained using toluene-3, 4-dithiol, but it was not found possible to liberate dithizone when 2-thionaphthol, n-hexane-thiol, dodecane-thiol or octadecane-thiol was used.

Saville[1] has stated that aqueous solutions of thiols, when treated with bromine, give the sulphonyl bromide, which can be converted to cyanogen bromide by reaction with cyanide ions. The cyanogen bromide can then be determined by Aldridge's method,[2] which is based on the von Braun reaction between pyridine and cyanogen bromide to produce an intermediate capable of condensing with benzidine to give a red product. A preliminary examination of the methods for the determination of thiols indicated that the method based upon Aldridge's procedure was the most promising.

EXPERIMENTAL

As a method was required for the determination of thiols in hexane solution, it was necessary to extract one of the reactants (*i.e.* thiol, sulphonyl bromide or cyanogen bromide) from the hexane to a solution so that the colour-producing reaction could be accomplished in an aqueous medium. It was found that isopropyl alcohol was the best solvent for the purpose.

In the first instance Saville's procedure was examined using a solution of n-hexane-thiol in isopropyl alcohol, and possible variations of the reaction conditions were investigated. Finally the procedure was applied to the determination of thiols in hexane solution.

Solutions

n-Hexane-thiol: 1 ml of n-hexane-thiol was dissolved in 250 ml of isopropyl alcohol to give a solution containing approximately 950 μg of SH/ml. From this stock solution, a working solution containing 1–1·5 μg of SH/ml was prepared by dilution with isopropyl alcohol.

Bromine water: 100 ml of water were added to 50 ml of saturated bromine water.

Phenol solution: 2% w/v of phenol and 5% of potassium bromide in water.

Potassium cyanide solution: 0·5% w/v in water.

Aldridge's reagent: Two solutions were prepared:

(*a*) 10 ml of concentrated hydrochloric acid added to 100 ml of constant boiling pyridine/water mixture.

(*b*) 1 g of benzidine hydrochloride dissolved in 20 ml of diluted (2 + 98 v/v) hydrochloric acid.

These two solutions were mixed when required. Any mixed solution unused after 3 days was discarded.

Measurements of optical density were made using either a Hilger and Watts "Spekker" absorptiometer or a Unicam Type SP500 spectrophotometer. Where figures are quoted in the text, the instrument used has also been recorded.

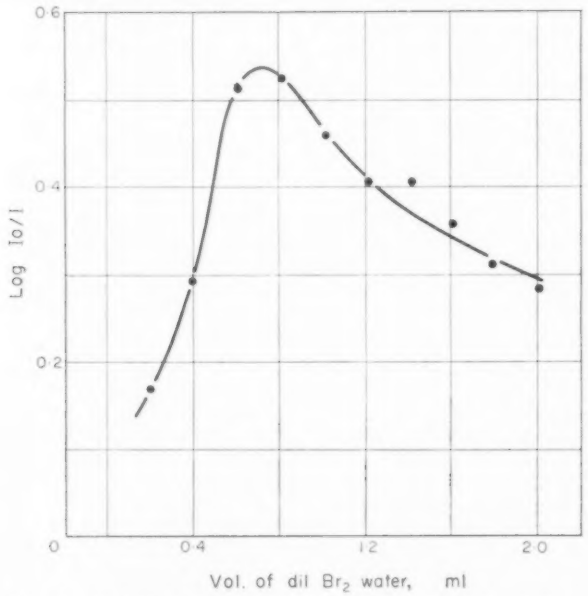

FIG. 1.—Variation of optical density of final solution in relation to the quantity of diluted bromine water used.

Method

One ml of the isopropyl alcohol solution of n-hexane-thiol containing 1–1·5 μg of SH was transferred to a 10-ml measuring flask, 1 ml of diluted bromine water was added, and the flask was shaken; 1 ml of phenol solution was added and the solution was shaken until the colour of bromine had disappeared; then 1 ml of potassium cyanide solution was added, followed by 5 ml of Aldridge's reagent. The optical density of the solution was then measured.

The amount of bromine and reaction time required

The quantity of bromine water used to oxidise the thiol compound was varied between limits of 0·2 and 2 ml, with the remaining conditions as outlined above. The results obtained are shown in Fig. 1.

The maximum value of optical density was given with approximately 0·7 ml of the diluted bromine water. In order to simplify the addition, a new dilution, of 50 ml of saturated bromine water to which

140 ml of water had been added, was prepared. Volumes of 1 ml of this new diluted solution were used for subsequent determinations.

It was noted that low values of optical density were obtained when diluted bromine solutions had been allowed to stand overnight. All such solutions were therefore freshly prepared each day.

It was also noted that if the bromine water was allowed to stand with the thiol reagent for a prolonged period of time, lower values of optical density were recorded. It was therefore necessary to establish the time interval for maximum values of optical density. This was done by using the arbitrary procedure noted above, with a variation of reaction time covering the range 0–14 min. The results obtained are given in Table I.

TABLE I.—VARIATION OF REACTION TIME
Unicam: 525 mμ, 4-cm cells

Reaction time, *min*	0	2	4	6	8	10	12	14
Log I_0/I	0·687	0·687	0·717	0·715	0·713	0·708	0·708	0·702

A reaction time of 5 min was adopted for subsequent work.

Selection of wavelength

Kodak No. 4 filters were used to obtain maximum values of optical density when measurements were made using the Spekker absorptiometer. An absorption spectrum of the red-coloured complex, obtained using the Unicam SP500 spectrophotometer is given in Fig. 2. The maximum absorption was given at a wavelength of 525 mμ.

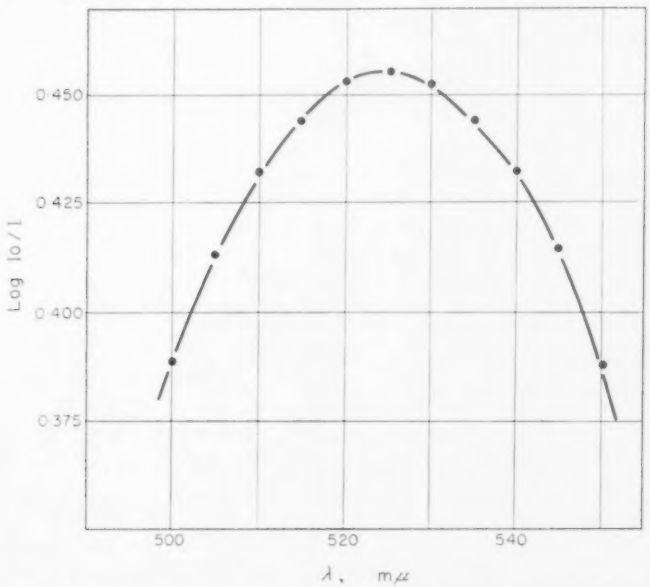

FIG. 2.—Absorption spectrum of the red complex given with Aldridge's reagent.

Variation in volume of sample aliquot

At normal room temperatures, bromine reacts slowly with isopropyl alcohol, and the optical densities obtained with Aldridge's reagent were found to depend upon the volume of alcohol used as solvent. In practice therefore, the volume of the isopropyl alcohol solution was kept at a constant value of 1 ml, and smaller aliquots were diluted to this volume before the addition of the diluted bromine water.

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Phenol solution

This solution is added to ensure the complete removal of the excess bromine before adding the potassium cyanide solution. It was found that 5–10 sec, with shaking, was a sufficient time for this reaction to take place, and that increasing this time resulted in low values of optical density, possibly caused by decomposition of the sulphonyl bromide. This is shown in Table II.

Table II.—Variation of reaction time following addition of phenol
Spekker: No. 4 filter, 1-cm cell

Reaction time, *sec*	5	10	60	120	180	240
Log I_0/I	0·564	0·564	0·558	0·531	0·523	0·518

Potassium cyanide solution

The cyanide solution reacts with the sulphonyl bromide to give cyanogen bromide. It was observed once again that the optical densities obtained with Aldridge's reagent depended upon the reaction time (Table III).

Table III.—Variation of reaction time following addition of cyanide solution
Unicam: 525 mμ, 2-cm cells

Reaction time, *sec*	10	30	60	120
Log I_0/I	0·250	0·351	0·342	0·214

The addition of Aldridge's reagent

It was noted that the reagent darkened in colour on keeping, but it was shown that for an age of up to 3 days this had no effect upon the final result, the optical density of the reagent blank solution being increased by the same amount as that of the sample solution. For maximum optical density a volume of about 4 ml of Aldridge's reagent was required. With smaller volumes, the colour was not fully developed, and it was difficult to accommodate larger volumes in the measuring flasks used (Table IV).

Table IV.—Volume of Aldridge's reagent required
Unicam: 524 mμ, 4-cm cells

Vol. of reagent, *ml*	2	3	4	5
Log I_0/I	0·838	0·923	0·936	0·932

On adding Aldridge's reagent to the solution, the red colour rapidly forms and the optical density reaches a maximum value after approximately 20 mins, and then slowly decreases. This is shown in Fig. 3. The optical densities of all coloured solutions were therefore measured 20 min after the addition of Aldridge's reagent.

Thiols in hexane solution

One of the requirements of the method is that the determination of the thiol should be made in hexane solution. As the reaction described does not take place in hexane, it is necessary to transfer one of the reacting species (*i.e.* thiol, sulphonyl bromide or cyanogen bromide) to an aqueous or alcoholic phase.

Attempts were made to evaporate the hexane solvent on a water bath, but in each case attempted, low values of optical density were obtained.

Isopropyl alcohol is miscible with hexane, and attempts were therefore made to produce a homogeneous solution containing hexane, thiol and isopropyl alcohol. On adding the bromine water the hexane separated, forming a separate phase; moreover the free bromine was rapidly removed from both phases. A solution of bromine in hexane was tried, but was found to be extremely unpleasant to use, difficult to standardise and very volatile.

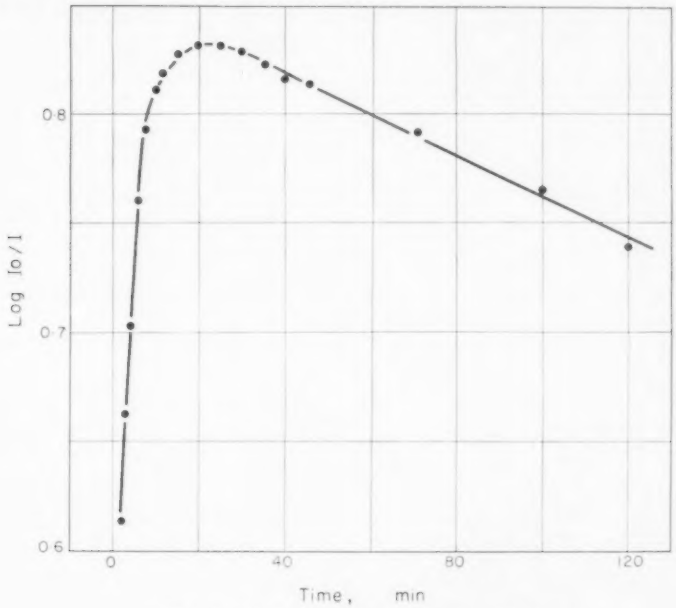

FIG. 3.—Variation of optical density with time:
● *n*-hexane-thiol
○ octadecane-thiol

On adding bromine water to the hexane solution, and shaking, most of the bromine is transferred to the organic layer, where the oxidation of the thiol to alkane sulphonyl bromide can then take place. This sulphonyl bromide can be extracted from the hexane phase into the aqueous phase by shaking with isopropyl alcohol. A measure of success was obtained using this procedure, which was therefore adopted as the arbitrary procedure from which variation of conditions was made.

Using the experience gained in the earlier work and using similar techniques it was possible to decide upon reaction times and reagent concentrations necessary to give maximum values of optical density. These are summarised below:

Bromine solution: The solution previously used for the alcoholic thiol solution, consisting of 5 volumes of saturated bromine water + 14 volumes of water, was found to give the maximum values of optical density. This solution was freshly prepared each day.

It was noted that inconsistent results were obtained with some dilute thiol solutions. This was attributed to some form of decomposition of the thiol before the addition of the bromine water. To prevent this, the order of addition of the thiol and bromine water was reversed, *i.e.*, the thiol was added to the bromine water. To ensure that no contaminating solution was left in the flasks used, they were left standing filled with dilute bromine water when not in use, and were washed out once with distilled water just before they were required.

Choice of solvent: A number of solvents were tried for the extraction of the alkane sulphonyl bromide from the hexane solution including acetone, industrial spirit, ethanol, dioxan and isopropyl alcohol. Of these the highest values of the optical densities of the coloured solutions were given when isopropyl alcohol was used.

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It was also noted that if the extraction time was prolonged, the excess of bromine disappeared and low results were obtained. The optimum results were obtained when 2·25 ml of alcohol were allowed to react for 1 min.

Cyanide solution: Again a reaction time of 0·5 min was found to be suitable.

Aldridge's reagent: As before, a volume of 4 ml and a reaction time of 25 min were found to give maximum densities.

Temperature: Using a constant temperature water bath, reaction tests were carried out in the range 18–30°. At the higher temperature slight decreases in maximum optical density were recorded, but in the range 18–25° these values remained constant.

Procedure

Reagents: These were prepared as described earlier in this paper, with the exception of the diluted bromine water for which a dilution of 5 volumes of saturated solution + 14 volumes of water was employed.

Method: Transfer by pipette 1 ml of the diluted bromine water into a clean 10-ml measuring flask and add 2 ml of the thiol in hexane solution, having a maximum concentration of 0·5 μg of SH/ml. Shake the flask, preferably mechanically, for 5 min, add 2·25 ml of isopropyl alcohol and shake for a further 1 min.

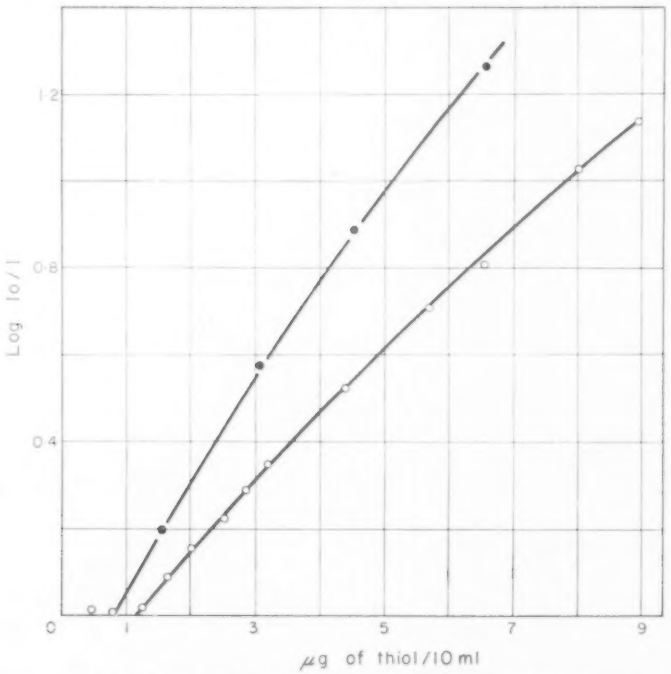

Fig. 4.—Calibration curves for *n*-hexane-thiol and octadecane-thiol: Unicam, 4-cm cells, 525 mμ.

Add 1 ml of phenol solution and shake by hand until all the colour of bromine has been discharged (a few sec only), add 1 ml of cyanide solution and shake, using the mechanical shaker, for 30 sec.

Add 4 ml of Aldridge's reagent and shake well by hand. After 15 min, remove the hexane layer with a pipette, dilute the solution to volume with distilled water, and mix well. Transfer the solution to a dry 4-cm spectrophotometer cell and allow to stand for about 7 min. The solution is usually slightly cloudy, but becomes clear on standing.

Measure the optical density using a spectrophotometer set at a wavelength of 525 mμ.

Calibration: In order to obtain calibration graphs, aliquots of diluted thiol solutions were examined by the procedure given above. These were prepared by dilution from concentrated thiol solutions standardised by titration with silver nitrate in an alcoholic ammoniacal medium with dithizone as indicator. This procedure is described by Kunkel *et al.*[4] Calibration curves for n-hexane-thiol and octadecane-thiol are shown in Fig. 4. These graphs indicate that the recovery of the thiol is not complete, possibly because of small quantities of alkane sulphonyl bromide remaining in the hexane layer. The quantities involved are: n-hexane-thiol, 0·92 μg (0·26 g of SH); octadecane-thiol, 1·36 μg (0·16 μg of SH).

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Zusammenfassung—Eine Methode zur Bestimmung von Thiolverbindungen in alkoholischen und Hexan-Lösungen im Konzentrationbereich 0·0005 bis 0·005 molar wird beschrieben. Die Methode folgt der von Saville beschriebenen, wonach die Thiolkomponente mittels Bromwasser zu einem Sulfonylbromid oxydiert wird. Auf Zusatz von Alkalicyanid formt dieses Bromcyan, welches sodann mit Aldridge's Reagens bestimmt wird.

Résumé—Les auteurs ont mis au point une méthode de dosage des thiols, dans des solutions d'alcool et d'hexane à des concentrations de 0,0005 M à 0,005 M. Cette méthode suit une technique décrite par Saville dans laquelle le thiol est oxydé en bromure de sulfonyle par l'eau de brome. Celui-ci, par addition de cyanure alcalin, forme du bromure de cyanogène qui est ensuite dosé en utilisant le réactif d'Aldridge.

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DIAMMONIUM-5,5′-INDIGO DISULPHONATE AS AN ANALYTICAL REAGENT

GRAVIMETRIC DETERMINATION OF THORIUM AND CERIUM^{III} AND THEIR SEPARATION FROM URANIUM^{VI}

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Summary—Diammonium-5,5′-indigo disulphonate forms insoluble complexes with many cations. Its use for the gravimetric determination of thorium and cerium^{III}, and their separation from uranium^{VI} has been investigated. Thorium and cerium^{III} are quantitatively precipitated within the pH range of 3·5 to 4·5 and 3·0 to 6·0 respectively, while uranium does not form any insoluble complex at this pH. The precipitate obtained in each case is ignited to the corresponding oxide and weighed.

INTRODUCTION

INDIGO carmine, the disodium salt of 5,5′-indigo disulphonic acid, has been used for the detection[1–13] and determination[1,14–22] of a large number of anions and cations. It has now been found that it also forms insoluble complexes with thallium^{I}, lead^{II}, calcium, barium, strontium, bismuth^{III}, yttrium, lanthanum, cerium^{III}, neodymium, samarium, dysprosium, zirconium^{IV}, thorium, molybdenum^{VI} and tungsten^{VI} from aqueous solutions of their salts.

The thorium and zirconium complexes are slightly soluble in water, and this leads to low results when they are washed with an excess of water. Because of the adsorption of sodium ions by the precipitate, an aqueous solution of the precipitant cannot be used as a wash liquid. This difficulty is avoided by using the diammonium salt of 5,5′-indigo disulphonic acid, the analytical behaviour of which is similar to that of indigo carmine.

For the determination of thorium, a large number of organic reagents have been reported in the literature,[23] but for its separation and determination in the presence of uranium there are few reagents which can be used successfully. Some of the important reagents which are suitable for this purpose are ferron,[24] *m*-nitrobenzoic acid,[25] anisic acid,[26] cinnamic acid,[27] *m*-cresoxyacetic acid,[28] sebacic acid[29] and 1-hydroxy-3-methoxyxanthone.[30]

The present authors find that diammonium 5,5′-indigo disulphonate, which is comparatively easy to prepare, can be successfully employed for the gravimetric determination of thorium at pH 3.5 to 4.5. Since the reagent does not form any insoluble complex with uranium even up to pH 9, it can be used for the separation of thorium from uranium.

There are only a few reagents which can be used for the determination of cerium alone or in the presence of other elements usually present in its minerals. The use of some of the common reagents, such as oxalic acid,[31] methyl oxalate[32] or potassium iodate,[33] is not convenient owing to the strict pH control which is necessary. Jefferson[34] used a number of organic bases but these do not offer any advantage over oxine.[35]

Though the results obtained with oxine are good, this reagent is not specific[36] and thus cannot effect the separation of cerium from uranium.

Diammonium 5,5′-indigo disulphonate has been found to precipitate cerium^{III} quantitatively in the pH range 3.0 to 6.0, and the results obtained are quite satisfactory. The determination of cerium when present alone or in the presence of uranium, up to about 10 times its amount, can readily be carried out.

EXPERIMENTAL

Preparation of the reagent

The method adopted for the preparation of diammonium 5,5′-indigo disulphonate was analogous to the one recommended[37] for the preparation of indigo carmine.

Five g of indigo (E. Merck, extra pure) with 55 ml of concentrated sulphuric acid (density 1·84) were heated in a water bath for about 1·5 hr, and then gradually poured into about 300 ml of cold water with constant stirring, and filtered hot. Solid ammonium carbonate was added to the filtrate till the ammonium salt of 5,5′-indigo disulphonic acid salted out. The mixture was then concentrated to about 250 ml and cooled in ice, and the diammonium 5,5′-indigo disulphonate was filtered off.

The product, on recrystallisation from hot water, weighed 6·20 g, and did not melt up to 360°.

Reagents and equipment

All the metallic salts used were either of B.D.H. (AnalaR) or E. Merck (Pro Analysi) grade.

An aqueous solution (1%) of the reagent was used as precipitant.

Hydrochloric acid, ammonia and glycine were used for adjustment of pH, which was measured with a Beckman pH Meter Model H2, using a suitable glass electrode.

Determination of thorium with diammonium 5,5′-indigo disulphonate

Two hundred and fifty ml of solution at pH 3·5–4·5, containing about 20 mg of thorium dioxide, were treated with 10 ml of a 10% aqueous solution of the reagent, with constant stirring. The mixture, on being kept at 80–90° for about 0·5 hr, produced a dark blue flocculent precipitate of the thorium complex, which, after cooling to room temperature, was filtered through Whatman No. 42 filter paper. The precipitate was washed with an aqueous solution (0·05%) of the reagent, dried, ignited and weighed as ThO_2.

Table I shows the results obtained with this reagent and those with oxine.

TABLE I.—DETERMINATION OF THORIUM

Wt. of ThO_2 present, *mg* (oxine method)	Wt. of ThO_2 found, *mg* (present reagent)
20·85	20·85
20·85	20·85
10·45	10·45
10·45	10·45
4·15	4·15
4·15	4·15

Effect of pH on the precipitation of the thorium complex

The effect of pH on the formation of the thorium complex with diammonium 5,5′-indigo disulphonate was studied by using ammonia and glycine as buffers for pH values higher than 3·5 and dilute hydrochloric acid for lower pH values. Though the reagent precipitates thorium in the range pH 1·0 to 7·5, the precipitation is quantitative only between pH 3·5 and 4·5.

Other common buffers containing acetate, phosphate and borate ions could not be used because of interference.

Determination of thorium in the presence of uranium^{VI}

Thorium in solutions containing varying quantities of uranium, was determined as described above. The results obtained are given in Table II.

TABLE II.—DETERMINATION OF THORIUM IN PRESENCE OF URANIUM

Wt. of ThO_2 taken, *mg*	Wt. of U_3O_8 present, *mg*	Wt. of ThO_2 found, *mg*
20·85	20·80	20·85
20·85	41·60	20·85
20·85	83·20	20·85
20·85	124·80	20·85
20·85	166·40	20·85
20·85	208·00	20·85

Determination of cerium^{III} *with diammonium 5,5′-indigo disulphonate*

To 200 ml of cerium^{III} solution (containing approximately 20 mg of CeO_2), at pH 5, about 10 ml of a 1% aqueous solution of the reagent was added with constant stirring. The resultant mixture was kept at 90° for about 0·5 hr and then cooled to room temperature. The blue flocculent precipitate was filtered through Whatman No. 42 filter paper. The precipitate was washed with an aqueous solution (0·05%) of the reagent, dried and ignited to the oxide. The results obtained are given in Table III.

TABLE III.—DETERMINATION OF CERIUM^{III}

Wt. of the CeO_2 present, *mg* (oxine method)	Wt. of the CeO_2 found, *mg* (present reagent)
19·75	19·75
19·75	19·75
9·90	9·90
9·90	9·90
5·00	5·00
5·00	5·00

Effect of pH on the formation of the cerium^{III} *precipitate*

The effect of pH (range 1·0 to 8·5) on the formation of the cerium^{III} complex was investigated using ammonia and glycine as buffers for pH values higher than 5·0 and hydrochloric acid for lower values. Though cerium^{III} is precipitated between pH 1·5 and 8·0, the precipitation is only quantitative between pH 3·0 and 6·0.

TABLE IV.—DETERMINATION OF CERIUM^{III} IN THE PRESENCE OF URANIUM^{VI}

Wt. of CeO_2 taken, *mg*	Wt. of U_3O_8 added, *mg*	Wt. of CeO_2 found, *mg*
19·75	20·80	19·75
19·75	52·00	19·70
19·75	104·00	19·75
19·75	156·00	19·75
19·75	208·00	19·75

Determination of cerium^{III} in the presence of uranium^{VI}

As the reagent does not form an insoluble complex with uranium^{VI}, even at pH 9·0, the determination of cerium^{III} in the presence of uranium^{VI} can readily be carried out.

Solutions of cerium^{III} containing varying amounts of uranium^{VI}, at pH 5·0, were taken and the determination of its cerium content was carried out using the reagent as described above. The results obtained are given in Table IV.

Investigations on the determination of zirconium, and on its separation from other elements with the help of this reagent are in progress.

Acknowledgement—The authors are much indebted to Prof. T. R. Seshadri, F.R.S., Head of the Chemistry Department, for his keen interest and helpful discussions during the course of the above investigations. Their thanks are also due to The Department of Atomic Energy, Government of India, for financial assistance.

Zusammenfassung—Diammonium-5-5′-indigodisulfonat bildet unlösliche Komplexe mit zahlreichen Kationen. Seine Anwendung zur gravimetrischen Bestimmung von Thorium und Cer(III) sowie zur Trennung der beiden von Uran(VI) wurde untersucht. Thorium und Cer(III) werden quantitativ gefällt im pH-Bereich 3·5–4·5 bzw. 3·0–6·0, während Uran in diesem Bereich keinen unlöslichen Komplex bildet. Die erhaltenen Niederschläge werde zu den entsprechenden Oxyden verglüht und gewogen.

Résumé—Le disulfonate de diammonium-5,5′-indigo forme des complexes insolubles avec de nombreux cations. Son utilisation pour le dosage gravimétrique du thorium et du cérium(III) et la séparation de ces derniers de l'uranium(VI) a été étudiée. Le thorium et le cérium(III) sont précipités quantitativement dans les domaines de pH: 3,5–4,5 et 3,0–6,0 respectivement, alors que l'uranium ne forme pas de complexes insolubles à ces valeurs de pH. Le précipité obtenu dans chaque cas est calciné pour former l'oxyde correspondant et pesé.

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ÜBER DIE ANWENDUNG VON CYSTEIN ALS MASKIERUNGSREAGENS BEI KOMPLEXOMETRISCHEN TITRATIONEN

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Zusammenfassung—Cystein bildet in schwach saurer Lösung mit einer Reihe von Kationen farblose, lösliche Komplexe. Die Komplexe mit Quecksilber und Kupfer sind stabiler als die entsprechenden Komplexe der Äthylendiamintetraessigsäure, was zur Maskierung der genannten Metalle bei komplexometrischen Titrationen ausgenützt wurde. Beschrieben ist die Bestimmung von Zn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Al^{3+} und Fe^{3+} in Gegenwart grösserer Mengen Quecksilber oder Kupfer bzw. die Bestimmung dieser zwei Metalle und der anderen angeführten Kationen nebeneinander.

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CYSTEIN bildet mit einer Reihe von Kationen sehr stabile Komplexe. Diese Eigenschaft des Cysteins wurde schon früher zu analytischen Zwecken ausgenützt. Beschrieben wurde z.B. schon eine Methode zur potentiometrischen Cysteinbestimmung mit Quecksilbernitratlösung,[1] sowie die volumetrische Bestimmung von Quecksilber und Nickel mit einer Cysteinlösung in alkalischem Medium.[2] Uns interessierte, ob sich die Bildung der Cystein-Metall-Komplexe nicht auch zur Maskierung mancher Kationen bei komplexometrischen Titrationen ausnützen liesse. Dabei zeigte sich, dass einige Metalle mit Cystein wirklich bedeutend festere Komplexe bilden als mit Äthylendiamintetraessigsäure, so dass diese Aminosäure bei einer Reihe von Bestimmungen mit Erfolg als Maskierungsreagens verwendet werden kann. Stabile Metallkomplexe bildet Cystein sowohl in alkalischen als auch in sauren Lösungen. In alkalischer Lösung sind die Verhältnisse jedoch sehr kompliziert, sodass hier noch ein weiteres Studium erforderlich ist.

In dieser Arbeit beschreiben wir vorläufig die Anwendung von Cystein als Maskierungsreagens bei Titrationen in saurer Lösung. Die im weiteren angeführten Ergebnisse zeigen, dass mit Cystein die Reihe der bisher bekannten Maskierungsreagenzien um einen neuen, interessanten und vorteilhaften Stoff bereichert wird.

REAKTIONEN DES CYSTEINS

In schwach saurer Lösung

Bei pH 5,5 reagiert Cystein mit Quecksilber unter Bildung eines weissen Niederschlages, der sich bei weiterer Zugabe von Cystein zu einer farblosen Lösung auflöst. Der sich bildende Komplex ist fester als der Quecksilberkomplex der Äthylendiamintetraessigsäure.

Thallium gibt mit Cystein eine braune Färbung. Durch weitere Zugabe von Cystein entsteht ebenfalls eine farblose Lösung. Hierbei handelt es sich jedoch um die Reduktion von Tl^{3+} zu Tl^{1+}. Da Tl^{1+} bei diesem pH nicht komplexometrisch bestimmt werden kann, lässt sich auch diese Reaktion zur Selektivitätserhöhung mancher Titrationen ausnützen.

Kupfer liefert mit Cystein erst eine schmutzigviolette Färbung, dann einen schmutzigen Niederschlag, der durch einen Überschuss von Cystein ebenfalls in eine

farblose Lösung übergeführt werden kann. Obwohl auch dieser Komplex fester ist als der Kupferkomplex der Äthylendiamintetraessigsäure, ist Cystein zur Maskierung von Kupfer nur beschränkt anwendbar. In Gegenwart anderer Kationen z.B. Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} entsteht nämlich nicht der farblose, lösliche Kupferkomplex, sondern es bilden sich verschiedenartig gefärbte Niederschläge. Diese Niederschläge wurden zwar nicht näher untersucht, höchstwahrscheinlich handelt es sich aber um Produkte, bei denen an Cystein ausser Kupfer auch noch das zweite Metall gebunden ist. Die Niederschläge sind in Wasser teilweise, in Komplexon vollständig löslich. Mit Komplexon können sie sogar sehr vorsichtig titriert werden; praktischen Wert hat so eine Titration allerdings nicht. Aus dem Gesagten geht hervor, dass Cystein zur Maskierung von Kupfer nur bei Rücktitrationen verwendet werden kann, wo der Komplexonüberschuss die Ausfällung der erwähnten Mischkomplexe verhindert.

Mit Cadmium gibt Cystein einen weissen Niederschlag, der durch weitere Zugabe von Cystein nicht vollkommen in Lösung gebracht werden kann. Aus dem Äthylendiamintetraessigsäurekomplex wird Cadmium durch Cystein nur unvollständig verdrängt. Daraus geht hervor, dass die Festigkeit des Cystein-Cadmium-Komplexes nicht von der Grössenordnung ist, die zu einer einwandfreien Maskierung notwendig ist.

Mit Wismut bildet Cystein einen löslichen, farblosen Komplex, der etwas fester ist als der Wismutkomplex der Äthylendiamintetraessigsäure. Der Unterschied in der Festigkeit beider Komplexe ist jedoch nicht gross genug um die einwandfreie Maskierung von Wismut zu garantieren.

Zink, Blei, Kobalt und Nickel bilden mit Cystein farblose, lösliche Komplexe. Aluminium und Eisen reagieren bei pH 2–3 mit Cystein ebenfalls unter Bildung löslicher Komplexe. Der Aluminiumkomplex ist farblos, der Eisenkomplex blau, seine Farbe wird jedoch mit der Zeit immer schwächer. Wird der pH-Wert der Lösung auf 5,5 eingestellt, so bleiben beide Kationen weiter als Komplexe in Lösung. Eisen bildet bei diesem pH-Wert ebenfalls einen farblosen Komplex. Die Komplexe aller dieser Kationen sind bedeutend schwächer als die entsprechenden Komplexe der Äthylendiamintetraessigsäure, so dass es möglich ist sie in Gegenwart von Cystein direkt oder indirekt mit Komplexon zu titrieren.

Die Reaktionen von namentlich nicht angeführten Kationen wurden nicht untersucht.

Auf Grund der beschriebenen Reaktionen kann gesagt werden, dass sich Cystein bei pH 5,5 zum Maskieren von Quecksilber in Gegenwart von Zink, Blei, Aluminium, Kobalt, Nickel und Eisen eignet. Störend wirken Cadmium und Wismut. Kupfer stört bei direkten Titrationen ebenfalls, bei Rücktitrationen kann es jedoch durch Cystein maskiert werden.

In alkalischer Lösung

Der Vollständigkeit wegen seien noch kurz die Reaktionen einiger Kationen mit Cystein in alkalischer Lösung angeführt.

Bei pH 11 bildet Cystein sehr feste farblose und lösliche Komplexe mit Quecksilber, Zink, Cadmium und Wismut. Alle diese Metalle können mit Cystein gegen Komplexon maskiert werden.

Blei bildet ebenfalls einen löslichen farblosen Komplex, der jedoch schwächer ist als der Bleikomplex der Äthylendiamintetraessigsäure. Cystein maskiert Blei nur gegen die Indikatoren Eriochromschwarz T oder Methylthymolblau.

Calcium, Barium, Magnesium, Aluminium und Mangan bilden mit Cystein entweder gar keine oder nur sehr schwache, farblose, lösliche Komplexe. Diese Metalle können in Gegenwart von Cystein direkt oder indirekt mit Komplexon titriert werden.

Kupfer bildet mit Cystein einen löslichen, intensiv braun gefärbten Komplex, der fester ist als der Kupferkomplex der Äthylendiamintetraessigsäure. Wegen der intensiven Farbe kann die Bildung dieses Komplexes jedoch nicht zur Maskierung von Kupfer ausgenützt werden. Die bekannte Blockierung von Eriochromschwarz T durch Kupfer lässt sich durch Zugabe von Cystein nicht verhindern.

Kobalt, Nickel und Eisen bilden mit Cystein Komplexe, deren Farbe und Festigkeit von der Reihenfolge abhängen, in der der Lösung Cystein, Puffer und eventuell Komplexon zugesetzt werden.

In alkalischen Lösungen treten einige Erscheinungen auf, die sich, ähnlich wie bei Kupfer in saurer Lösung, am besten durch Bildung von Mischkomplexen erklären lassen. So lassen sich z.B. Cadmium und Zink in Gegenwart von Magnesium oder Mangan nicht mit Cystein maskieren, obwohl beide Metalle für sich allein so feste Cysteinkomplexe bilden, dass die Maskierung möglich ist. Diese Erscheinungen erschweren selbstverständlich die praktische Anwendung von Cystein zum Maskieren in alkalischen Lösungen; sie sind Gegenstand weiterer Untersuchungen.

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EXPERIMENTELLER TEIL

Reagenzien

Die 0,05 M-Komplexon-(III)-Lösung wurde auf bekannte Weise hergestellt.

Die 0,05 M Lösungen von Hg^{2+}, Tl^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Bi^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+} und Al^{3+} wurden aus den entsprechenden Nitraten bzw. Sulfaten (Reinheit p.a.) hergestellt. Alle Lösungen waren schwach mit Salpetersäure angesäuert. Die Titer aller Lösungen wurden komplexometrisch kontroliert.

Das verwendete l-Cystein war ein Erzeugniss der Fy. Lachema, Brno. Es wurde den Lösungen in fester Form zugesetzt.

Xylenolorange kam als 0,5% ige wässrige Lösung zur Anwendung.

Als Pufferlösung wurde eine 20%ige wässrige Urotropinlösung verwendet.

Analysenbeispiele

1. *Die Bestimmung von* Zn^{2+} (Pb^{2+}) *in Gegenwart von* Hg^{2+}: Die schwach saure Lösung wird mit 10 ml einer 20%igen Urotropinlösung versetzt. Weiter werden Cystein und einige Tropfen Xylenolorange zugegeben. Nun wird mit 0,05 M Komplexonlösung bis zum Auftreten der gelben Farbe titriert. Der Verbrauch an Komplexonlösung entspricht dem Zink- oder Bleigehalt.

2. *Die Bestimmung von* Zn^{2+} (Pb^{2+}) *und* Hg^{2+} *nebeneinander:* Zuerst wird in mit Urotropin gepufferter Lösung die Summe der Kationen durch direkte Titration gegen Xylenolorange bestimmt. Dann wird der Lösung Cystein zugesetzt und das freigewordene Komplexon, dass dem Quecksilber gehalt entspricht, wird mit 0,05 M Bleinitratlösung titriert. Der Farbumschlag verläuft hierbei von reingelb nach blauviolett.

3. *Die Bestimmung von* Co^{2+} (Ni^{2+}, Al^{3+}, Fe^{3+}) *in Gegenwart von* Hg^{2+} (Cu^{2+})*:* Die saure Lösung (pH 2–3) wird mit einem Überschuss der 0,05 M Komplexon(III)-Masslösung versetzt. Dann wird Cystein zugeben. Der pH-Wert der Lösung wird nun mit Urotropin auf 5,5 eingestellt und nach Zugabe einiger Tropfen Xylenolorange wird mit 0,05 M Bleinitratlösung zurücktitriert. Die Menge des nicht zurücktitrierbaren Komplexons entspricht dem Kobalt-, Nickel-, Aluminium-oder Eisengehalt Sollen die angeführten Kationen neben Kupfer bestimmt werden, so empfiehlt es sich, die Titration in der Wärme durchzuführen. Die Verdrängung des Kupfers aus dem Äthylendiamintetraessigsäurekomplex durch Cystein verläuft in der Kälte nämlich etwas zu langsam. Bei Titrationen in der Wärme ist es der besseren pH-Einhaltung wegen vorteilhafter anstelle des normalen Urotropinpuffers

Urotropin- oder Acetatpuffer mit Salpetersäurezusatz zu verwenden (z.B. eine Lösung von 140 g Urotropin und 120 ml 1 N HNO_3 oder 200 g Natriumacetat und 150 ml 1 N HNO_3 in 1 Liter Wasser). Auf die beschriebene Weise kann neben Kupfer auch Zink oder Blei bestimmt werden.

4. *Die Bestimmung von* Co^{2+} (Ni^{2+}, Al^{3+}, Fe^{3+}) *und* Hg^{2+} (Cu^{2+}) *nebeneinander:* Die saure Lösung (pH 2–3) wird mit einem Überschuss der 0,05 M Komplexon(III)-Masslösung versetzt. Der pH-Wert der Lösung wird nun mit Urotropin auf 5,5 gebracht und nach Zugabe einiger Tropfen Xylenolorange wird der Überschuss des Komplexons mit 0,05 M Bleinitratlösung retitriert. Auf diese Weise wird die Summe der Kationen bestimmt. Nun wird Cystein zugegeben und das freigewordene Komplexon, das dem Quecksilber-, oder Kupfergehalt entspricht wird mit 0,05 M Bleinitratlösung weitertitriert. Aus Gründen, die schon im vorigen Beispiel angeführt wurden, ist es auch hier bei Kupferbestimmungen empfehlenswert in der Wärme zu arbeiten und Pufferlösungen mit Salpetersäurezusatz zu verwenden. Auf gleiche Weise können auch Zink oder Blei und Kupfer nebeneinander bestimmt werden.

DISKUSSION

Cystein eignet sich bei komplexometrischen Titrationen in schwach sauren Lösungen zum Maskieren von Quecksilber. Cadmium und Wismut stören. Kupfer stört bei direkten Titrationen ebenfalls, bei Rücktitrationen kann es jedoch mit Cystein maskiert werden. In Tabelle 1 sind die Ergebnisse einiger Analysen zusammengestellt, die unter Zuhilfenahme von Cystein als Maskierungsreagens durchgeführt wurden. Aus der Tabelle geht hervor, dass bei diesen Analysen die gleiche Genauigkeit ereicht wird, wie bei anderen komplexometrischen Titrationen.

TABELLE I.—KOMPLEXOMETRISCHE BESTIMMUNG EINIGER KATIONEN IN SCHWACH SAURER LÖSUNG BEI ANWENDUNG VON CYSTEIN ALS MASKIERUNGSREAGENS.

Analysen-vorschrift	gegeben, *mg*	gefunden, *mg*
1	Pb 103,6 Hg 200,6	Pb 103,8
2	Zn 6,5 Hg 100,3	Zn 6,5 Hg 100,5
3	Co 11,8 Hg 40,1 Fe 14,0 Hg 40,1 Ni 15,0 Cu 6,3 Zn 19,5 Cu 12,6	Co 11,7 Fe 13,9 Ni 15,2 Zn 19,5
4	Ni 15,0 Hg 80,2 Co 14,7 Cu 12,6 Fe 8,4 Cu 15,9 Pb 20,8 Cu 31,8	Ni 14,9 Hg 80,3 Co 14,7 Cu 12,7 Fe 8,4 Cu 15,8 Pb 20,6 Cu 31,9

Vergleichen wir Cystein mit Thiosemikarbazid, das von Körbl und Přibil[3] zur Maskierung von Quecksilber in schwach sauren Lösungen empfohlen wurde, dann sehen wir, dass sich beide Stoffe gut ergänzen. In Gegenwart von Eisen ist es z.B. nicht gut möglich Quecksilber mit Thiosemikarbazid zu maskieren; Cystein dagegen kann sehr wohl angewendet werden. Cadmium und Wismut dagegen machen das Arbeiten mit Cystein unmöglich, während sie die Anwendung von Thiosemikarbazid nicht stören.

Kupfer kann mit Cystein zwar nur bei Rücktitrationen maskiert werden, es sind

aber hier einige Bestimmungen möglich (z.B. Cu und Fe, Co oder Ni nebeneinander), die früher nur auf kompliziertere Weise[4] durchgeführt werden konnten.

Erfolgversprechend ist auch die kombinierte Maskierung von Kationen mit Cystein und anderen Maskierungsreagenzien. Als Beispiel seien o-Phenanthrolin[5] oder α,α'-Dipyridyl[6] genannt, die in schwach saurer Lösung ausser Blei und Aluminium fast alle in Frage kommenden Kationen maskieren.

Noch nicht zufriedenstellend gelöst ist die Anwendung von Cystein als Maskierungsreagenz bei komplexometrischen Titrationen in alkalischer Lösung. Diese Möglichkeit wird jedoch von uns weiter verfolgt.

Summary—In weakly acid solutions cysteine forms colourless soluble complexes with a series of cations. The complexes with mercury and copper are more stable than the corresponding complexes with ethylenediaminetetra-acetic acid, so that they can be used for masking purposes in complexometric titrations of these ions. The determination of Zn^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+} and Fe^{3+}, in the presence of larger amounts of mercury or copper, and of these last two and the series of ions listed in the presence of one another.

Résumé—En solution faiblement acide, la cystéine forme des complexes incolores solubles avec une série de cations. Les complexes avec le mercure et le cuivre sont plus stables que les complexes correspondants avec l'acide éthylènediaminetétracétique, de sorte qu'ils peuvent être utilisés comme agents complexants dans les titrages complexométriques de ces ions. On peut doser Zn^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+} et Fe^{3+} en présence de grandes quantités de mercure ou cuivre, ainsi que ces deux derniers et la série des ions énumérés en présence de chaque autre.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM WITH 3,3′-DIAMINOBENZIDINE

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Summary—A simple, rapid and highly selective method for determining small amounts of vanadium has been developed based on the oxidation of diaminobenzidine with vanadate ion. The reaction is best carried out in a phosphoric acid medium. The molar ratio of the reaction was found to be 1:1. The sensitivity and molar absorptivity of the method were found to be 0·016 μg of vanadium per cm^2 for log $I_0/I = 0{\cdot}001$, and 3,310, respectively.

INTRODUCTION

THIS paper describes a new spectrophotometric method for the determination of small amounts of vanadium, based on an oxidation colour reaction of 3,3′-diaminobenzidine (DAB) with vanadate ion in an acidic medium. The rate of oxidation is dependent upon the acid concentration and the kind and quantity of acid present. The acid concentration is not critical, however, when phosphoric or perchloric acid is employed. Because versatile and sensitive analytical methods for determining small amounts of vanadium are not abundant, the use of DAB as an analytical reagent for vanadium was investigated.

DAB has been proved to be an excellent reagent for selenium.[1,2] Hoste[2] first reported a qualitative test for vanadium using DAB, and later Cheng[1] pointed out that vanadate^V oxidised DAB in the presence of EDTA (ethylenediaminetetra-acetic acid) in a weakly acidic medium; so far, however, no quantitative procedure for vanadium which uses DAB has appeared in the literature. Because of its high selectivity and fair sensitivity, an attempt to develop a quantitative method for vanadium, utilising the colour reaction, was undertaken.

APPARATUS

Beckman Model DU spectrophotometer equipped with 1-cm cells.

REAGENTS

Standard vanadium solution: Prepared from ammonium metavanadate, 50 μg per ml.

Phosphoric acid: 85% (density = 1·80).

3,3′-Diaminobenzidine tetrachloride (DAB) solution: Freshly prepared before use, 1×10^{-2} *M*. The pure reagent is snow white in colour. Some of the material on the market showed a reddish or purplish colour caused by air oxidation. It should be kept in a refrigerator under an inert atmosphere. The properly stored material is indefinitely stable.

Other reagents used were analytical reagents.

Preparation of calibration curve

To a solution containing 25–250 μg of vanadium in a 25-ml calibrated flask add 1 ml of 85% phosphoric acid and dilute to approximately 20 ml with water. Cool, add 1 ml of 10^{-2} *M* DAB solution (freshly prepared), make to the mark with water, and mix. Measure the absorbance at 470 mμ, using a reagent blank, after standing for 15 min.

DEVELOPMENT OF METHOD

Absorption spectra

The oxidation product of DAB by vanadate is reddish-brown and has three absorption maxima at 340, 380, and 470 mμ. The DAB solution is slowly oxidised by air and shows similar maxima (Fig. 1). The maximum of 470 mμ was chosen for all measurements in this study.

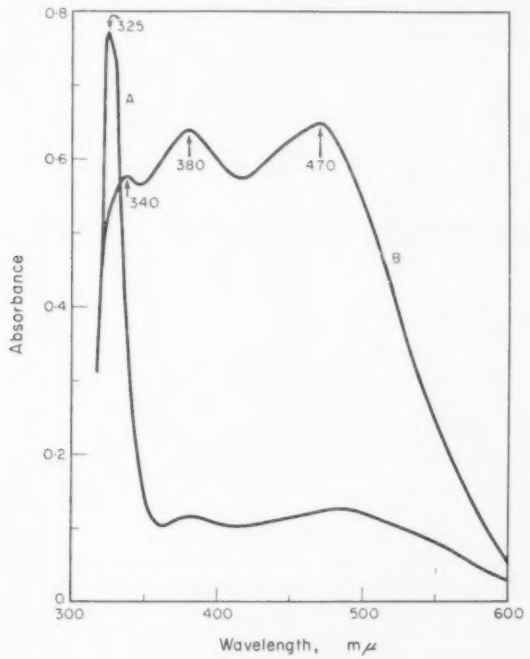

FIG. 1.—Absorption spectra.
A—DAB ($10^{-5}M$) oxidised by air for 2 days in 0·3M H_3PO_4.
B—25 μg of vanadium + 0·01 mmole of DAB + 15 mmoles of H_3PO_4.
Total volume 25 ml: 1-cm cell.

Effect of acidity

The colour reaction is best carried out in a solution containing 0.02–0.2 ml of 85% phosphoric acid per ml volume. More phosphoric acid may be added, but if this is done a calibration curve using the same amount of phosphoric acid should be prepared. The reaction may also be carried out in the presence of EDTA, which is used as a masking agent, at pH 2–3, but the colour develops rather slowly in a less acidic medium. The curves in Fig. 2 indicate that both phosphoric acid and perchloric acid can be used over a wide range of acid concentrations, without significant effect, and that only limited amounts of other acids should be present because they may decrease the colour intensity. Their inhibiting effect may be attributed to the change in the oxidation potential of vanadate in different acid media. For a 25-ml volume, 10 ml of glacial acetic acid completely masked the colour development. Small amounts of tartaric or citric acid also masked the colour reaction, because of reduction of vanadate, or complex formation. The use of phosphoric acid is preferred, because it gives maximum colour development independent of its concentration, and also because it

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complexes iron^{III} giving a colourless solution, and preventing the iron^{III} from oxidising DAB.

Effect of amount of DAB

The curves in Fig. 3 show that 10 μmoles of DAB are sufficient for less than 300 μg of vanadium. Actually the excess amount of DAB has no effect on the blank because the freshly prepared solution is colourless. These curves also indicate a 1: 1 reaction between DAB and vanadate.

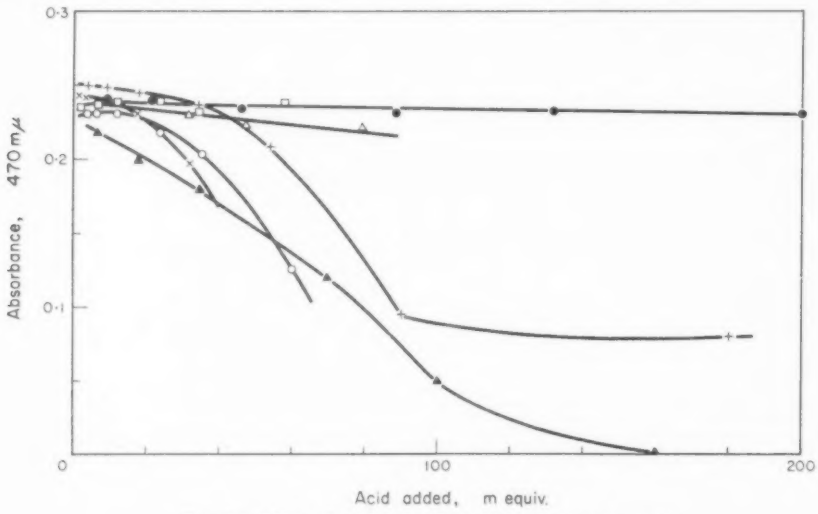

FIG. 2.—Effect of acid on oxidation of DAB with vanadate.
□—$HClO_4$: ●—H_3PO_4: △—HNO_3:
○—HCl: +—H_2SO_4: ▲—HOAc: ×—HBF_4.

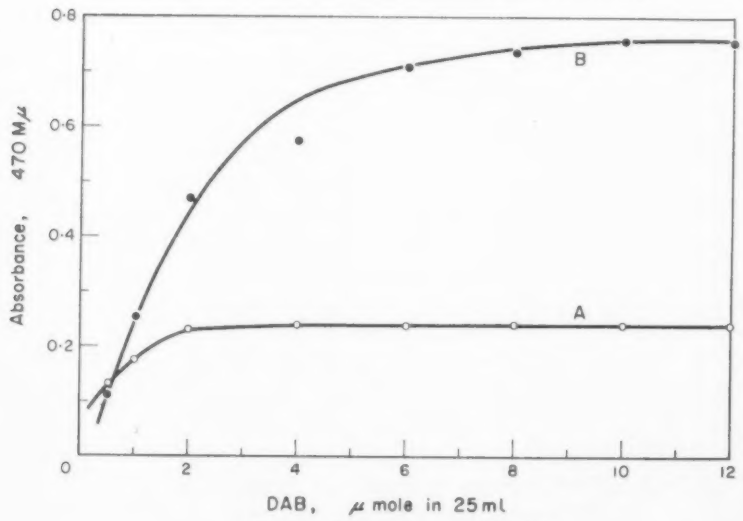

FIG. 3.—Effect of amount of DAB.
A—2μ moles of vanadium.
B—6μ moles of vanadium.

Beer's law

Beer's law was followed for 1–25 μg of vanadium per ml in a phosphoric acid medium, as shown in Fig. 4. At pH 2.5 the colour development was slow, especially for low concentrations of vanadium, because the oxidation potential of vanadate ion to vanadyl ion decreases with decrease in acidity. Furthermore, the rate of oxidation

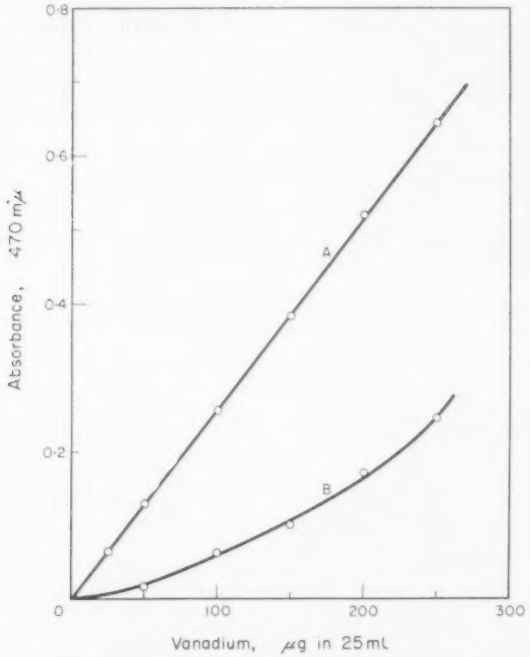

FIG. 4.—Calibration curve.
A—1 ml of 85% phosphoric acid added: standing for 15 min.
B—0·025 mmole of EDTA added, pH 2·5: standing for 30 min.

is probably influenced by the catalytic action of the intermediate products as evidenced by the much slower colour development of lower concentrations of vanadium. Maximum colour development may be obtained when the solutions are allowed to to stand for 2 hr or longer.

Stability

The colour reaction developed rapidly in a phosphoric acid medium. It is recommended that the absorbance be measured after standing for 15 min. After standing for 1 hr the absorbance shows no significant change. Any unnecessary delay in measurement of absorbance should, however, be avoided, because air slowly oxidises DAB. Therefore a reagent blank should always be made.

Sensitivity

The DAB reaction for vanadium is fairly sensitive. The sensitivity is 0.016 μg of vanadium per cm^2 for log $I_0/I = 0.001$. The molar absorptivity is 3,310. The DAB method is more sensitive than the classic hydrogen peroxide method.

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INTERFERENCES

Cations

DAB, like other amines, is easily oxidised; hence any strong oxidising reagent interferes. For example, chromium^{VI} interferes but chromium^{III} does not. Highly coloured solutions interfere, however; with weakly coloured solutions the interference may be eliminated by correction with a sample blank. According to Hoste, in the absence of oxidising agents the DAB reaction is specific for vanadium^{V}. The interference of iron^{III} can be eliminated by phosphoric acid or by pyrophosphate. Large amounts (say, 0.1 g) showed some interfering effect, however, even in the presence of 5 ml of 85% phosphoric acid. It seemed that there was sufficient iron^{III} ion dissociated from the ferric-phosphate complex to oxidise DAB. When a sample is dissolved in hydrochloric acid or a mixture of hydrochloric acid and nitric acid, vanadium can be oxidised to vanadate, but cerium, manganese, or chromium cannot be oxidised to the highest oxidation state by nitric acid. Under ordinary conditions, the DAB reaction for vanadium seems to be highly selective. The results shown in Table I were

TABLE I.—DETERMINATION OF VANADIUM IN PRESENCE OF FOREIGN METALS

(100 μg of vanadium taken in 25 ml)

Metal present*	Vanadium found, μg
Iron^{III}	102·2
Chromium^{III}	97·4
Titanium^{IV}	98·5
Niobium^{V}	100·0
Tantalum^{V}	100·5
Tin^{IV}	97·8
Molybdenum^{VI}	99·2
Zirconium^{IV}	100·2
Copper^{II}	100·5
Tungsten^{VI}	100·2
Manganese^{II}	100·0

* The amount present was 1×10^{-2} mmole, except for iron when it was 10 mg.

obtained when vanadium was determined in the presence of the metals which are often present with vanadium or which interfere in the methods commonly used for vanadium. These results are satisfactory. Amounts of iron^{III} as large as 10 mg did not interfere. For unusual amounts of iron, it may be necessary to separate by electrolysis,[3] solvent extraction, or ion exchange[4] before attempting the vanadium determination. Traces of selenium produced no significant effect; large amounts interfere and may be separated by solvent extraction.[1] The oxidation product of DAB is not extracted by benzene or toluene.

Anions

As shown in Fig. 2, the solution should contain mainly phosphate or perchlorate anions; small amounts of other anions are tolerable, but large amounts of the other anions shown in Fig. 2 should be removed. This is easily done by evaporating the solution to dryness or nearly so, then evaporating again with phosphoric acid. Addition of organic acids should be avoided, because they may complex vanadium, or may

reduce it to its lower oxidation state, which does not oxidise DAB. Both tartrate and citrate masked the vanadate reaction with DAB; the former reduced vanadate ion, and formed a strongly coloured yellow complex. Fluoride showed no effect; therefore, for special occasions, it may be advantageous to add fluoride as a masking agent. For instance, tantalum is more easily hydrolysed than niobium; it is difficult to keep tantalum in solution in phosphoric acid medium. Addition of fluoride helps to do this. Hydrogen peroxide did not oxidise DAB in a phosphoric acid medium, but it did inhibit colour development by forming a stable peroxy complex with vanadium.

COMPARISON OF DAB WITH RELATED COMPOUNDS

The colour development of vanadate with 3,3′-diaminobenzidine may be made in a wide range of concentrations of phosphoric or perchloric acid. Nitrate does not oxidise the reagent. The reproducibility is excellent. The reagent solution containing phosphoric acid remains colourless even when allowed to stand for more than 10 hr. Sulphate and tungstate form no precipitates with the reagent in a strongly acidic medium.

Diphenylamine and its sulphuric acid derivative are oxidised by nitrate.[5] The reproducibility is poor.[6] Diphenylbenzidine is also oxidised by nitrate, and colour development with vanadate requires a high concentration of phosphoric acid.[7] The interference arising from precipitation by sulphate and tungstate is serious. 3,3′-Dimethylnaphthidine often gives a colour in the blank. The slow colour development may be improved by using a mixture of phosphoric acid and perchloric acid, but a high concentration of acid is necessary for maximum colour development.[8] Poor reproducibility in the determination of vanadium in steel has been reported.[9]

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Zusammenfassung—Eine einfache und hochselektive Schnellmethode zur Bestimmung kleiner Vanadinmengen wurde entwickelt. Die Methode beruht auf der Oxydation von Diaminobenzidin durch Vanadationen. Die Reaktion verläuft am besten in phosphorsaurem Medium. Es wurde gefunden, dass das Molverhältnis der Reaktanten 1:1 ist. Die Empfindlichkeit der Reaktion ist 0·016 μg V per cm² für 0·001 Absorption. Der molare Extinktionkoeffizient beträgt 3310.

Résumé—L'auteur a mis au point une méthode simple, rapide et très sélective de dosage de faibles quantités de vanadium. Cette méthode est basée sur l'oxydation de la diaminobenzidine par l'ion vanadate. La réaction est réalisée dans les meilleurs conditions en milieu acide phosphorique. Le rapport molaire de la réaction est 1/1. La sensibilité et le coefficient d'extinction molaire sont respectivement 0,016 μg de vanadium par cm² pour $\log I_0/I = 0{,}001$, et 3310.

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GRAVIMETRIC DETERMINATION OF TUNGSTEN BY HOMOGENEOUS PRECIPITATION*

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Summary—A homogeneous precipitation method has been developed for the gravimetric determination of tungsten, by thermal decomposition of soluble peroxytungstate from a nitric acid-hydrogen peroxide solution. It appears that in all cases, especially for small concentrations, the tungsten recovery is superior to the classical techniques using cinchonine or β-naphthoquinoline. Furthermore, co-precipitation of molybdenum and vanadium are reduced to a considerable extent. The study of the co-precipitation process shows that the distribution coefficients follow a linear pattern for both contaminants. The method has been tested with good results on a number of standard tungsten alloy steels, corrections for incomplete precipitation and co-precipitation being applied on the basis of the experimentally found values.

THE gravimetric determination of tungsten usually involves the use of organic reagents such as cinchonine or β-naphthoquinoline to ensure a quantitative precipitate of tungstic acid.

Leliaert, Hoste and Eeckhaut[1] recently proposed a homogeneous precipitation method for tungstic acid, by thermal decomposition of soluble peroxytungstic acid from a hydrogen peroxide medium. A quantitative precipitate was not required in this case, as an isotope dilution technique was used. From preliminary experiments[2] it appeared, however, that this method is capable of giving quantitative results, co-precipitation of molybdenum and vanadium being considerably reduced.

Radioactive tracer techniques were used to develop the proposed method.

Radio-isotopes

Tungsten: ^{187}W, β, γ-emitter, half life 24 hr, produced by irradiation of WO_3 in the BR-1 reactor.

Molybdenum: ^{99}Mo, β, γ-emitter, half life 67 hr, produced by irradiation of molybdic oxide in the BR-1 reactor.

Vanadium: ^{48}V, β, γ-emitter, half life 16 d, produced by 22 MeV deuteron bombardment of titanium. ^{48}V was separated, carrier-free, according to Irvine and Schindewolf.[3]

Counting techniques

Integral γ-counting was used for ^{187}W and ^{48}V using a well-type NaI(T1) detector. Because the daughter ^{99}Te interferes with γ-counting of ^{99}Mo, β-counting with an end-window G.M. tube was used for ^{99}Mo after separation as MoS_3.

Homogeneous precipitation of tungsten

Upon acidifying a standardised sodium tungstate solution with a mineral acid, incomplete precipitation of tungstic acid occurs. The resulting precipitate can be redissolved by adding an adequate amount of hydrogen peroxide, a soluble peroxy-acid being formed.

When this solution is heated, the excess of hydrogen peroxide and the peroxytungstic acid are decomposed, causing a homogeneous precipitation of tungstic acid.

Preliminary experiments showed that, in HNO_3 medium, optimum results were obtained by adding an equal volume of HNO_3 (60%) to the aqueous solution of the tungstate, and by redissolving the

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precipitate with 1 ml of H_2O_2 (30%). Thermal decomposition took place on heating the solution at 60° for 90 min, after which the precipitation was complete.

Homogeneous precipitation from other mineral acid solutions is less successful. Thermal decomposition in an $HClO_4$ medium, for instance, proceeded very slowly in the presence of large amounts of $HClO_4$, so that only 5 ml of $HClO_4$ (70%) could be used per 25 ml of tungsten solution. Even then a heating period of 2 hr at 80° was required before the decomposition was complete.

The decomposition in H_2SO_4 (10 ml of 98% acid per 25 ml of tungsten solution) also proceeded slowly, so that a temperature of 110° was necessary during 4 hr.

In all the experiments the amount of tungsten left in solution was computed by adding, before the acid, 500 μl of ^{187}W tracer of known activity (approx. 1×10^6 cpm) and counting an aliquot of the filtrate.

The results are summarised in Table I. Results by precipitation with cinchonine and β-naphthoquinoline are included for comparison.

TABLE I.—QUANTITATIVE CHARACTER OF THE TUNGSTEN PRECIPITATION

W/25 ml, *mg*	Tungsten left in solution, %*				
	HNO_3	$HClO_4$	H_2SO_4	Cinchonine	β-naphtho-quinoline
251·08	0·13	0·60	4·03	0·44	0·13
100·5[6]	0·11[5]	0·91	6·39	0·37	0·47
50·9[9]	0·10	0·72	4·87	1·42	0·96
20·8[7]	0·51	1·40	13·76	1·37	3·38
10·8[3]	0·66[5]	1·90	18·13	4·82	5·33

* Average of 2 experiments.

From Table I it appears that homogeneous precipitation of tungsten from a nitric acid solution gives highly satisfactory tungsten recoveries. At the highest tungsten concentrations investigated, the recovery is identical to that with β-naphthoquinoline whereas at low concentrations, the former proves to be far superior (99·34% instead of 95%).

Homogeneous precipitation from a perchloric acid medium is somewhat less satisfactory, although it is still superior to precipitation with the organic reagents.

Homogeneous precipitation from a sulphuric acid medium, on the other hand, is unacceptable. Losses of up to 20% occur at the higher dilutions investigated.

Co-precipitation of molybdenum and vanadium

It is well known that in the presence of molybdate and vanadate, large amounts of Mo and V co-precipitate with tungstic acid. It might be expected that homogeneous precipitation would reduce this co-precipitation to a considerable extent.

Conditions for minimum co-precipitation of molybdenum were examined by varying the temperature, and consequently the decomposition rate of the peroxytungstate. In all the experiments the amount of molybdenum co-precipitated was determined by measuring the ^{99}Mo activity left in solution.

The results for solutions containing 50 mg of tungsten (as tungstate) and 15 mg of molybdate are summarised in Fig. 1.

It appears that the co-precipitation increases if a decomposition temperature higher than 60° is chosen. The experiments showed that at this temperature a heating period of 1·5 hr is required to achieve complete thermal decomposition of the peroxytungstate.

The co-precipitation of molybdenum was investigated for molybdenum/tungsten

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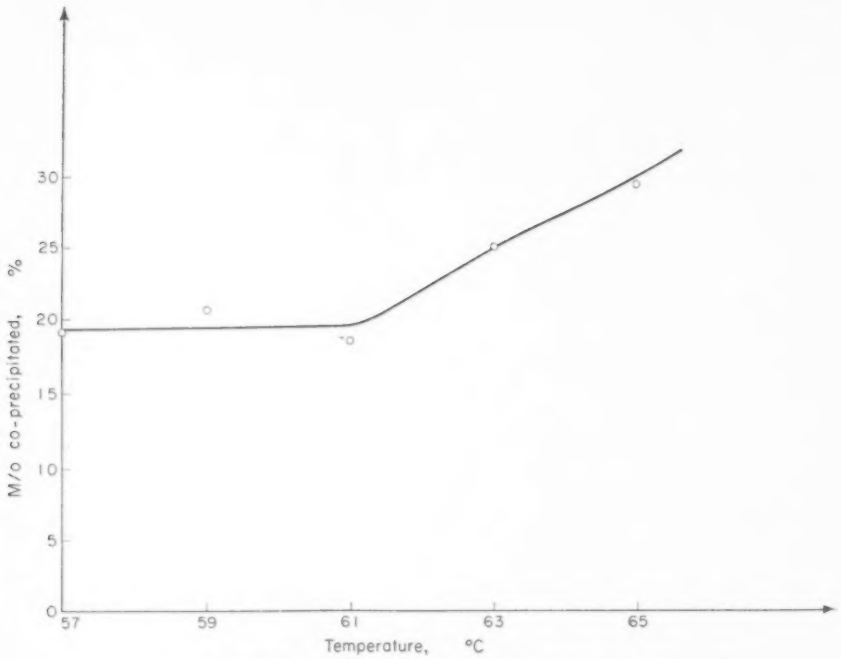

FIG. 1.—Molybdenum co-precipitated as a function of temperature.

ratios varying from $3{\cdot}5 \times 10^{-3}$ to 1×10^{2}; the vanadium/tungsten ratio was varied from $1{\cdot}6 \times 10^{-3}$ to 50. The absolute amount of tungsten precipitated varied between 251 mg for small ratios, down to 5 mg for larger ratios.

The results for molybdenum are summarised in Table II.

Results for the co-precipitation of molybdenum using β-naphthoquinoline are given by Leliaert (*loc. cit.*) and are presented for comparison in Table III.

It is apparent that the co-precipitation of molybdenum is reduced to a considerable

TABLE II. CO-PRECIPITATION OF MOLYBDENUM
(homogeneous precipitation)

W, *mg*	Mo, *mg*	Mo/W ratio	Mo co-precipitated, %	Error on W, %
251	0·64	$3{\cdot}53 \times 10^{-3}$	93·3	0·28
251	1·25	$4{\cdot}95 \times 10^{-3}$	88·2	0·53
251	2·22	$9{\cdot}10 \times 10^{-3}$	90·0	0·95
251	5·15	$2{\cdot}08 \times 10^{-2}$	90·6	2·22
251	10·3	$4{\cdot}18 \times 10^{-2}$	73·9	3·62
251	22·2	$8{\cdot}85 \times 10^{-2}$	49·0	5·16
50·1	11·2	$2{\cdot}25 \times 10^{-1}$	27·9	7·35
50·1	22·2	$4{\cdot}5 \times 10^{-1}$	22·9	12·0
$10{\cdot}0^{2}$	12·5	1·25	12·4	17·10
$5{\cdot}0^{1}$	52·3	$1{\cdot}04 \times 10$	9	—
$5{\cdot}0^{1}$	502	$1{\cdot}01 \times 10^{2}$	3·2	—

extent, although the induced error is far from negligible in the case of large Mo-W ratios.

The co-precipitation of vanadium was studied in the same experimental conditions as for molybdenum, using ^{48}V tracer. The results as summarised in Table IV, the data given by Leliaert using β-naphthoquinoline being presented in Table V.

TABLE III.—CO-PRECIPITATION OF MOLYBDENUM
(β-naphthoquinoline procedure)

Mo/W ratio	Mo co-precipitated, %
0·15	80
0·3	65
1·17	32
2·35	26

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TABLE IV.—CO-PRECIPITATION OF VANADIUM
(homogeneous precipitation)

W, *mg*	Mo, *mg*	V/W ratio	V co-precipitated %	error on W, %
251	0·40	$1·6 \times 10^{-3}$	5·8	0·02
251	1·00	4×10^{-3}	5·2	0·03
251	2·00	8×10^{-3}	4·8	0·05
251	5·00	2×10^{-2}	4·5	0·13
251	10·0	4×10^{-2}	4·3	0·24
251	20·0	8×10^{-2}	3·8	0·43
251	50·0	2×10^{-1}	2·7	0·76
100·2	50·0	5×10^{-1}	1·6	1·05
100·2	100	1	1·1	1·44
50·1	250	5	0·35	2·4
5·0[1]	250	$5·0 \times 10^{1}$	less than 0·3	less than 20

TABLE V.
CO-PRECIPITATION OF VANADIUM
(β-naphthoquinoline)

V/W ratio	V co-precipitated, %
0·01	10
0·1	7·5
0·2	7
0·5	5·2
1·0	3·5
2·0	2·8

It is apparent that the vanadium co-precipitation is also considerably reduced by homogeneous precipitation, and is smaller than the co-precipitation of molybdenum by an order of magnitude.

Determination of the distribution coefficients

It is well known that in co-precipitation phenomena three types of distribution occur between solid and liquid phase. Linear distribution following Nernst's law can occur according to equation (1):

$$\frac{x}{a-x} = D\,\frac{y}{b-y} \tag{1}$$

where x and y represent the respective amounts of carrier and co-precipitant separated, a and b the initial concentrations.[4]

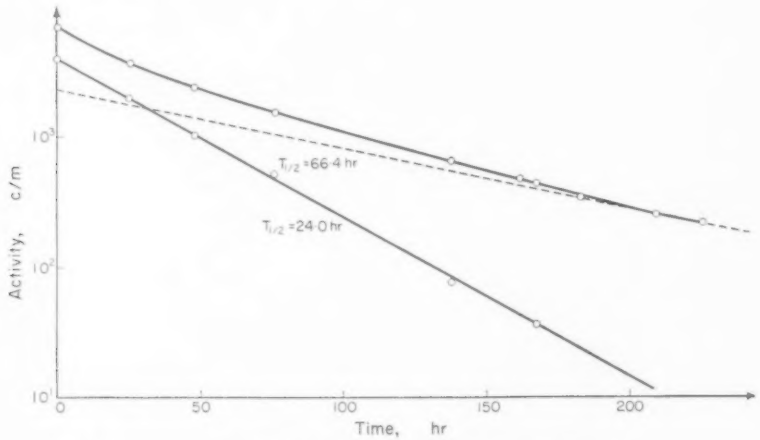

FIG. 2.—Analysis of ^{187}W–^{99}Mo decay curve.

In the second case Doerner and Hoskins[5] law is observed, following the logarithmic distribution of equation (2):

$$\ln\frac{a}{a-x} = \lambda\,.\,\ln\frac{b}{b-y} \tag{2}$$

In the third case the amount of co-precipitant is linear with the amount of precipitated carrier. This type of distribution was first observed by R. Mumbrauer,[6] and a quantitative interpretation of it was given by Hahn,[7] while the distribution law was deduced by Riehl[8] to be equation (3):

$$\frac{x}{y} = K\,.\,\frac{a}{b} \tag{3}$$

In the present case, tracer techniques offer a relatively simple means of determining the amount of co-precipitant as a function of the amount of precipitated carrier. To effect this, a small quantity of solution was removed at regular intervals. Since the half-lives of ^{187}W and of ^{99}Mo or ^{48}V are sufficiently different, the amount present of each element may be computed by analysis of the composite decay curve, after extrapolation to time t_0

Typical decay curves are given in Figs. 2 and 3.

Procedure: In a 400 ml conical flask are placed successively 100 ml of tungstate solution (10 mg of W/ml), 1 ml of molybdate (10 mg of Mo/ml) or 1 ml of vanadate (2 mg of V/ml), 100 ml of HNO_3 (60%), 5 ml of H_2O_2 (30%), 4 ml of ^{187}W tracer and 4 ml of ^{99}V tracer. The activities of the tracer solutions were chosen to correspond to approximately $1{\cdot}5 \times 10^5$ cpm of each tracer in the Mo co-precipitation experiments, and $1{\cdot}7 \times 10^6$ cpm in the case of V.

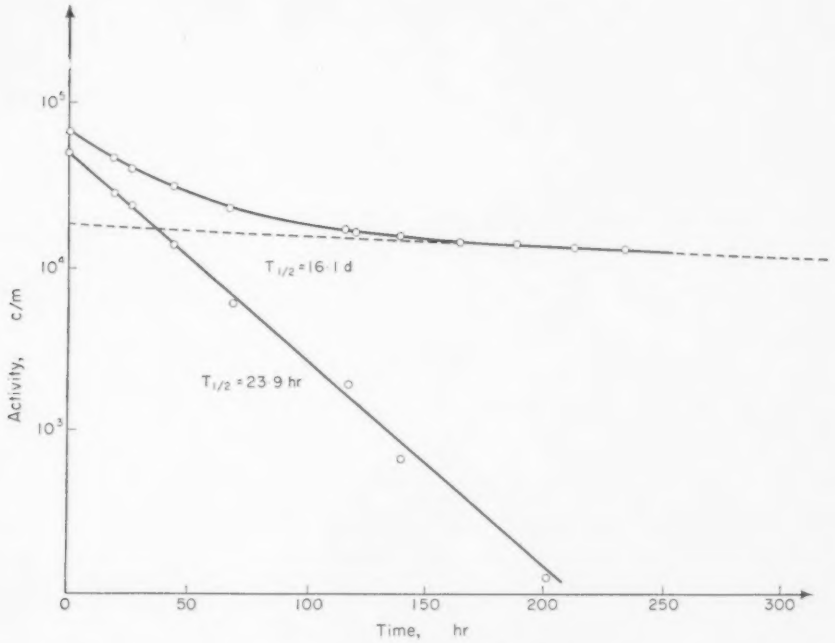

FIG. 3.—Analysis of ^{187}W–^{48}V decay curve.

The solution was heated in a thermostat at 60° and 5 ml portions of solution were removed by reverse filtration through an asbestos filter at 5-min intervals.

In the case of molybdenum, the isotopes are measured by G.M. counting, to avoid interference from ^{99}Tc daughter activity. The filtrates were therefore diluted to 50 ml, neutralised to pH2 with ammonia, and precipitated as their sulphides with thioacetamide, and the collected sulphides were mounted on standard planchettes and measured with the G.M. counter.

In the case of vanadium, 4 ml of the filtrates were counted in standard vials in a well-type NaI(Tl) detector.

The results are presented in Fig. 4, curve 1 (Mo) and curve 2 (V).

The values of D, λ and K computed according to equations (1), (2) or (3) are represented in Table VI.

From Table VI it appears that Riehl's law is followed in both cases; the amounts of co-precipitants are directly proportional to the amounts of precipitated carrier, the mean values being $K_{Mo} = 1{\cdot}34$ ($\pm 0{\cdot}09$) and $K_V = 14{\cdot}4$ ($\pm 2{\cdot}6$).

According to the views of Hahn this type of distribution does not involve true homogeneous mixed crystal formation, the process rather being caused by surface layer crystallisation, with continuous diffusion from the solution into the crystal body.

TABLE VI.—CO-PRECIPITATION OF MOLYBDENUM WITH TUNGSTEN

W pptd, %	Mo co-pptd, %	Distribution coefficients		
		D	λ	K
17·4	13·4	0·73	0·75	1·30
27·3	21·2	0·72	0·75	1·29
29·0	24·1	0·78	0·80	1·20
44·2	27·2	0·47	0·55	1·62
54·1	34·1	0·44	0·54	1·48
58·2	43·2	0·55	0·65	1·35
70·1	54·1	0·50	0·65	1·30
80·2	60·8	0·38	0·58	1·32
90·1	69·7	0·26	0·58	1·29
90·8	76·4	0·33	0·69	1·20

CO-PRECIPITATION OF VANADIUM WITH TUNGSTEN

W pptd, %	V co-pptd, %	Distribution coefficients		
		$D \times 10^2$	$\lambda \times 10^2$	K
25·6	2·1	6·2	7·1	12·1
30·3	2·2	5·2	6·0	13·7
41·2	3·9	5·8	7·5	10·5
42·5[5]	2·3	3·2	7·1	18·5
43·1	4·0	5·5	7·2	10·8
54·7	4·4	3·8	5·7	12·4
63·7	4·0	2·4	4·0	15·9
77·8	4·2	1·3	2·9	18·5
88·7	4·9	0·7	2·3	18·1
92·1	6·1	0·5[6]	2·1	15·1
92·8	7·5	0·6[3]	3·0	12·4

Determination of tungsten in alloy steels

The determination of tungsten by homogeneous precipitation was tested on a number of N.B.S. and British Standard Steels. The results obtained were corrected for incomplete tungstic acid recovery (Table I), silicon content (given by the certificates), molybdenum and vanadium content (Table II and III respectively). Double homogeneous precipitation was used for Mo-W ratios larger than unity.

Procedure: A suitable amount of steel turnings (1–2 g) is treated with 30 ml of 11N HCl in a 400-ml beaker. The solution is heated on a hot plate below the boiling point until the reaction subsides, Then 20 ml of 14N HNO_3 are added dropwise. If tungsten carbide particles remain undissolved, 10 ml of $HClO_4$ (70%) are added and the solution is taken to near dryness. The residue is treated with 25 ml of 14N HNO_3 and is again taken to dryness, and the process is repeated to insure a complete removal of the hydrochloric acid. The residue is treated with 50 ml of water, 2 ml of H_2O_2 (30%) and 50 ml of 14N HNO_3. If large amounts of silica are present, the insoluble residue is removed by filtration and the silicon correction is not applied. The solution is heated in a thermostat at 60° for 1·5 hr. As soon as the precipitate has settled, the hot solution is filtered (fine porosity paper), washed with hot 1% HNO_3 and incinerated at 800° for 1 hr.

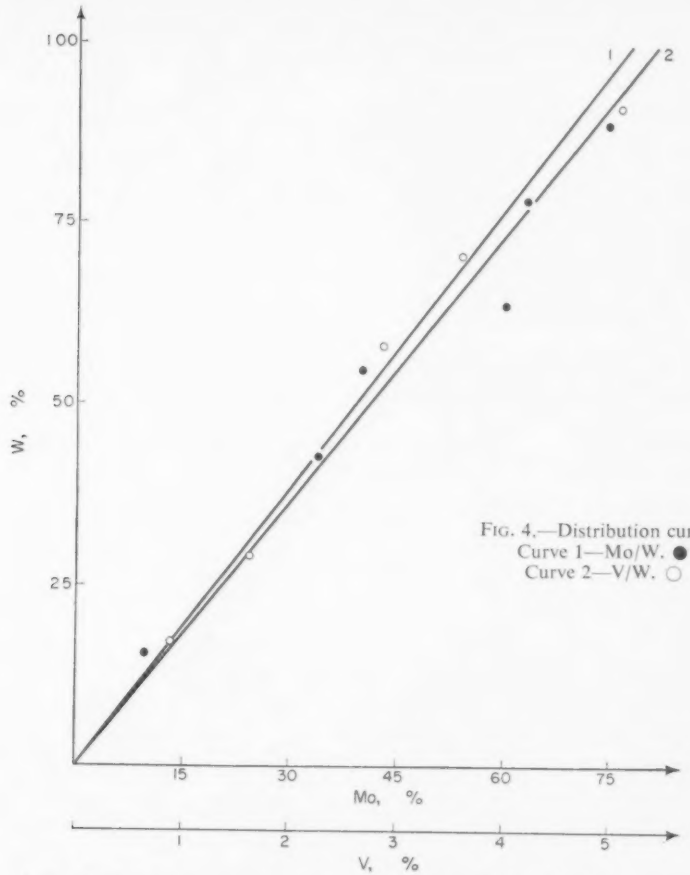

FIG. 4.—Distribution curves.
Curve 1—Mo/W. ●
Curve 2—V/W. ○

TABLE VII.—DETERMINATION OF TUNGSTEN IN STANDARD STEELS

N.B.S steels	W, %	Stand. deviation,* %	Mo/W ratio	Sample size, g	W after 1st precipitation, %	W after 2nd precipitation,	Mean, %	W after correction, %	Deviation from certificate, %
153	1·58	1·5	5·2	2·0015	—	1·54[1]	1·56[1]	1·56[4]	−1·0
				2·0009	—	1·58[1]			
132A	6·20	1·1	0·73	2·0023	7·23	—	7·21	6·17[5]	−0·4
				2·0006	7·19	—			
155	0·517	1·3	0·075	2·0038	0·526	—	0·525	0·505	−2·4
				2·0006	0·524	—			
50 C	18·44	0·4	0·0044	1·0094	18·93	—			
				1·0008	18·82	—	18·88	18·30	−0·7[5]
				1·0012	18·88	—			
Tool steel 440/880	13·0	—	0·0054	1·5230	13.27	—			
				1·5024	13·23	—	13·23	12·90	−0·7
				1·5026	13·19	—			
B.C.S 241/1	19·61	0·4[5]	0·026	1·0007	20·16	—	20·21	19·49	−0·6
				0·9992	20·25	—			

* The standard deviation was computed from the values given in the respective certificates.

NBS 153: C 0·864; Mn 0·219; P 0·025; S 0·008; Si 0·187; Cu 0·099; Ni 0·107; Cr 4·14; V 1·04; Mo 8·39; W 1·58; Co 8·45.
NBS 132A: C 0·825; Mn 0·268; P 0·029; S 0·006; Si 0·190; Cu 0·120; Ni 0·137; Cr 4·21; V 1·94; Mo 4·51; W 6·20.
NBS 155: C 905; Mn 1·25; P 0·015; S 0·010; Si 0·322; Cu 0·083; Ni 0·100; Cr 0·485; V 0·014; Mo 0·039; W 0·517.
NBS 50C: N 0·012; As 0·022; Sn 0·018; C 0·719; Mn 0·342; P 0·022; S 0·010, Si 0·311; Cu 0·079; Ni 0·069; Cr 4·13; Cr 4·13; V 1·16; Mo 0·082; W 18·44.
NBS Tool Steel: 440/880: C 0·7; Mn 0·15; Si 0·14; Cu 0·059; Cr 2·12; V 2·11; Mo 0·070; W 13·0; Co 11·8.
BCS 241/1: Sn 0·025; C 0·85; Mn 0·295; P 0·021; S 0·033; Si 0·33; Cu 0·10; Ni 0·075; Cr 5·03; V 1·57; Mo 0·52; W 19·61; Co 5·67.

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The results are summarised in Table VII. From this it appears that the results are in good agreement with those of the certificates, the deviation from the given values being within 1 %, except for NBS steel No. 155. The larger deviation in this case is obviously caused by the fact that with a 2-g sample a precipitate of only 15 mg of WO_3 is obtained.

Zusammenfassung—Wolfram wird gravimetrisch bestimmt, nach Fällen aus homogener Lösung durch thermische Zersetzung des löslichen Peroxywolframates in Salpetersäure-Wasserstoffperoxyd-Lösung. Es scheint, dass in allen Fällen, besonders für niedere Konzentrationen, die neue Methode den klassischen Verfahren unter Verwendung von Cinchonin oder β-Naphthochinolin überlegen ist. Weiters is die Mitfällung von Molybdän und Vanadin beträchtlich reduziert. Mitfällungsstudien zeigten, dass die Verteilungsfaktoren für beide Verunreinigungen ein lineares Verhalten aufweisen. Die Methode wurde an einer Anzahl von Standardstählen erprobt, wobei für Unvollständigkeit der Fällung und Mitfällung von Verunreinigungen Korrekturen angebracht wurden, deren Grösse aus experimentellen Befunden erhalten werden konnte. Die Resultate waren sehr zufriedenstellend.

Résumé—Les auteurs ont mis au point une méthode de précipitation homogène pour le dosage gravimétrique du tungstène, par décomposition thermique de peroxytungstate soluble obtenu à partir d'une solution acide nitrique-eau oxygénée. Il apparaît que dans tous les cas, et spécialement pour de faibles concentrations, la récupération du tungstène est supérieure à celle obtenue par les techniques classiques utilisant la cinchonine ou la β-naphtoquinoleine. De plus, la coprécipitation du molybdène et du vanadium est concidérablement réduite. L'étude du processus de coprécipitation a montré que les coefficients de partage suivent une loi linéaire pour les deux impuretés. La méthode a été essayée, donnant de bons résultats, sur un certain nombre d'aciers spéciaux standard au tungstène; les corrections de précipitation incomplète et de coprécipitation, basées sur les valeurs expérimentales, ont été appliquées.

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ANALYTICAL USE OF ARSENAZO III

DETERMINATION OF THORIUM, ZIRCONIUM, URANIUM AND RARE EARTH ELEMENTS

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Summary—The reagent arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid]) gives marked colour reactions with a number of elements. Anions affect the reaction only to a slight degree and it is possible to work at low pH values; the reaction is very sensitive and the compound can thus be used for the photometric determination of Th, Zr, Hf, U, rare earths, and some other elements. The method is most selective for Th, Zr and U^{IV}. Materials containing these elements can be analysed directly, in the solutions formed after dissolving the sample, without separation of the stable elements.

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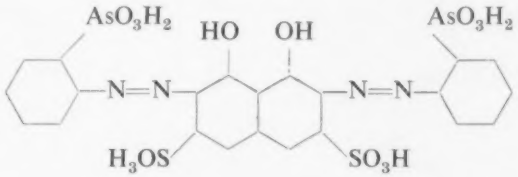
AZO-DYES based on chromotropic acid are widely used as reagents for the photometric determination of various elements. Especially useful and universally applicable are reagents containing the arsonous group-AsO_3H_2. Such a reagent was first prepared by Kuznetsov[1] in 1941 and named, in its abbreviated form, "arsenazo". Various improved analogues of arsenazo were sythesised later and also tested; these included arsenazo II (which is a double molecule of arsenazo)[2] and arsenazo III, a bis-diazo dye based on chromotropic acid and *o*-aminophenylarsonic acid.[3] The latter compound, 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid], is especially suitable for the photometric determination of thorium, zirconium, uranium^{IV} and of some other elements.



ARSENAZO III

The properties of arsenazo III

Arsenazo III is generally obtained in the form of its disodium salt; it is a crystalline, dark-red powder, soluble in water or in weak acids, readily soluble in water which has been rendered alkaline with sodium bicarbonate or sodium carbonate, and insoluble in concentrated acids, or in solutions saturated with sodium chloride, acetone, alcohol or ethyl ether. The reagent is stable in its dry as well as in its dissolved form; its properties do not change even when stored for long periods. Oxidising agents (H_2O_2, Cl_2, Br_2) and strong reducing agents ($Na_2S_2O_3$, Ti^{III}) attack the reagent; therefore solutions in which the elements are to be determined must be freed of oxidising and reducing agents. Usually this does not present any serious difficulties.

The colour of the aqueous solutions of arsenazo III depends on the pH of the medium. The solutions are pinkish or red-crimson coloured, depending on the concentration, within the pH limits of 4 to 10*N* hydrochloric acid, *i.e.* under conditions usual for the determination of most elements; a 0.01–0.1% aqueous solution of arsenazo III is generally used. In the alkaline region, at pH 5 and higher, a violet or blue colour is observed; the colour is green in concentrated sulphuric acid.

Colour reactions with elements

Colour reactions of arsenazo III at various acidities conform to the general rules for the effect of the pH on the colour of the reaction products obtained with colour reagents.[4] Arsenazo III gives colour reactions with many elements (Table I). Its basic characteristic property consists in its ability to form stable chelates; elements can therefore be determined in strongly acidic media and in the presence of sulphates, fluorides, phosphates, oxalates and other complex-forming anions which generally inhibit the direct determination of elements.

TABLE I.—COLOUR REACTIONS OF ARSENAZO III

Element	Conditions of determination	Colour of complex	Elements inhibiting the determination
Reagent alone	4–10*N* HCl	Pinkish–crimson	
Th	0·01–10*N* HCl	Green	—*
U^{IV}	0·05–10*N* HCl	Green	Th*
Zr	0·2–10*N* HCl	Green	Th
UO_2^{2+}	pH 4–pH 1	Green	Zr, rare earths, Ca†
Sc	pH 4–pH 1	Violet	Th, Zr, U, Ca, Cu,
Y, La and lanthanides	pH 4–pH 3	Green	Th, Zr, U, Ca, Cu,
Bi	pH 4·5–pH 1·5	Violet–blue	Many elements‡
Pb	pH 5–pH 4	Blue	Many elements‡
Fe^{III}	pH 3–pH 1·5	Lilac–violet	Many elements‡
Cu	pH 5–pH 4	Blue	Many elements‡
Ba	pH 5–pH 4·5	Violet–blue	Many elements‡
Ca	pH 5–pH 4	Blue	Many elements‡

* In the presence of oxalic acid for masking zirconium.
† In the presence of Trilon B and potassium fluoride, for masking thorium and other elements.
‡ The possibility of selective determination of these elements was not investigated in detail.

Photometric determinations in strongly acidic media are useful in many cases; difficulties caused by the partial hydrolysis of ions of the elements to be determined are eliminated; it is no longer necessary to maintain carefully the pH with the aid of buffer solutions; the selectivity of determination is increased for a number of elements, *etc.* The slight effect of anions makes it possible to use direct methods of determination in many cases, *i.e.* direct photometric determination can be carried out without separating sulphates, phosphates and other admixtures.

The sensitivity of the colour reactions is of a sufficiently high degree (0.05 to 0.01 μg/ml of the element) when using a spectrophotometer or a photocolorimeter. Quantities of 0.5 μg/ml or more of the element can be determined by visual methods. The methods are most sensitive for the determination of thorium, zirconium, uranium, the rare earth elements and less sensitive for lead, bismuth, iron, copper, calcium, barium.

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The high selectivity of the colour reactions is coupled with a well defined contrast in colour transition from pinkish (reagent) to blue or even emerald green (complexes of arsenazo III with elements) and with a high stability of the corresponding arsenazo III complexes; this makes it possible to attain high degrees of dilution without dissociation of the complex. The form of the curves—absorption spectra of the reagent and the complex—is especially important when using photometers. A considerable shift of the absorption spectrum of the complex is observed towards the long wavelengths (compared to the absorption spectrum of the reagent) as well as two sharply defined peaks on the curve of the light-absorbing complex (Fig. 1); this phenomenon makes

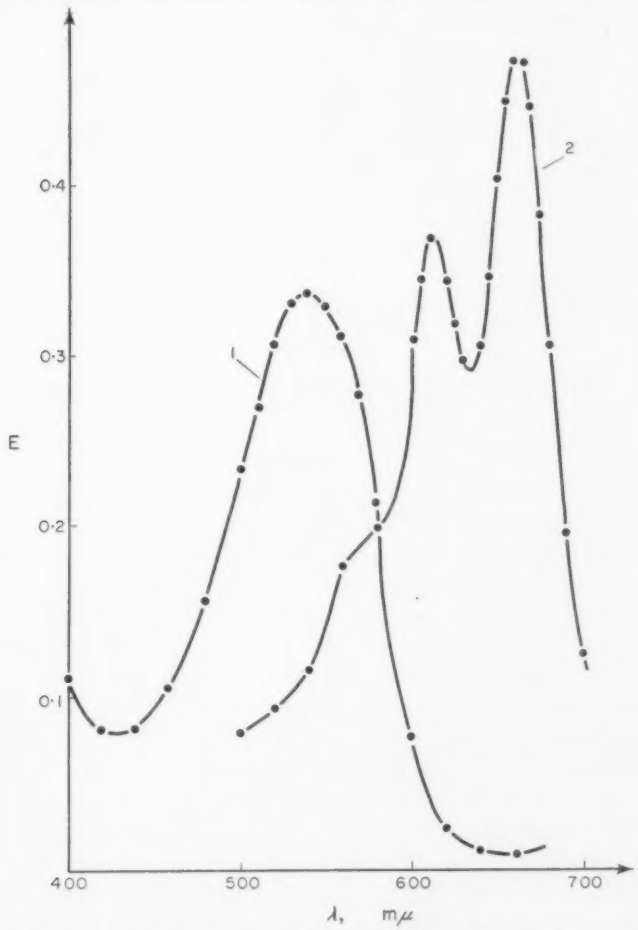

FIG. 1.—Absorption spectrum of arsenazo III and of its thorium complex:
1. $0{\cdot}9 \times 10^{-5}M$ arsenazo III in $4N$ HCl;
2. $0{\cdot}9 \times 10^{-5}M$ arsenazo III and $2{\cdot}5 \times 10^{-5}M$ $Th(NO_3)_4$ in $4N$ HCl;
(Spectrophotometer SF–4, 10 mm cell).

it possible to attain maximum sensitivity during the determination of the element when working at the optimum wavelengths of 660 to 665 mμ. Furthermore, the reagent itself, present in considerable excess during the determination, does not influence the reaction when using this wavelength. A red-light filter is generally used when working

with photocolorimeters; in this case the excess reagent is eliminated almost completely. The coefficients of molar extinction of some systems are listed in Table II.

TABLE II.—SENSITIVITY OF COLOUR REACTIONS OF ARSENAZO III

Element	Conditions of max. sensitivity of reaction	Coefficient of molar extinction, ε*	Sensitivity, $\mu g/ml$	
			Spectrophotometer, 50 mm cell	Visual
Th	9*N* HCl, λ 665 mμ	130,000	0·01–0·02	0·5–1
Zr	9*N* HCl λ 665 mμ	120,000	0·01–0·02	0·5–1
Hf	9*N* HCl λ 665 mμ	~95,000	0·02	1–2
U^{IV}	4*N* HCl λ 670 mμ	100,000	0·02	1–2
UO_2^{2+}	pH 2·0 λ 665 mμ	53,000	0·02	1–2
Sc	pH 1·7 λ 675 mμ	19,000	0·05	3–4
Y	pH 3·0 λ 655 mμ	55,000	0·02	1–2
La	pH 3·0 λ 655 mμ	45,000	0·02	1–2
Ce	pH 3·0 λ 655 mμ	47,000	0·02	1–2
Gd	pH 3·0 λ 655 mμ	58,000	0·02	1–2
Tb	pH 3·0 λ 655 mμ	62,000	0·02	1–2
Yb	pH 3·0 λ 655 mμ	49,000	0·02	1–2
Zn	pH 3·0 λ 655 mμ	43,000	0·02	1–2
Ca	pH 5·0 λ 655 mμ	~10,000	0·05–0·1	3–5
Pb	pH 5·0 λ 655 mμ	10,000	0·05–0·1	3–5

* Calculated according to the formula $\varepsilon = \frac{E}{cl}$. The method of saturation at excess reagent was used (*cf. e.g.* Fig. 4). For rare earths, data according to [15].

Selectivity

Arsenazo III (Table I) gives colour reactions with many elements and, consequently is not specific for any element.

Its selectivity, *i.e.* to determine any element in the presence of others, can therefore only be increased by using specific methods. The simplest method appears to be the determination of the required acidity of the solution.

The region of optimum pH values for the interaction of organic colour reagents with elements is known to vary for various elements. The distinct analogy between colour reactions and hydrolysis reactions should be noted.[5] Thus colour reactions with colour reagents are given in strongly acidic media only by those elements whose ions readily tend to hydrolyse: zirconium, hafnium, uranium^{IV}, thorium; in mildly acidic media the reactions also yield colours with iron^{III}, uranyl ion, rare earths; in mildly acidic media and in neutral media only with: calcium, strontium, magnesium.

Finally, the reaction conditions (optimum pH) are directly related and depend on the nature of the reagents used in the reaction. But for each reagent the ratio of optimum pH values of the reaction with elements remains always constant: easily hydrolysed elements interact in a very acidic medium, stable elements in less acidic media. This also holds true for the reagent arsenazo III.

It can be seen that a high degree of selectivity is attained when determining quadrivalent elements—zirconium, hafnium, thorium, uranium^{IV}—with arsenazo III; this reaction can be carried out in strongly acidic media, of the order of 2–10*N* hydrochloric acid ; stable elements do not inhibit the reaction. But the determination of uranium^{VI}, rare earths and of other elements is inhibited by many elements.

The degree of selectivity can also be increased by other methods apart from varying the acidity of the mixture. Frequently it is recommended to bind the inhibitors into a colourless stable complex. This is only possible when the element to be determined and the admixtures form with the masking, complex-forming compound—under the the given conditions (at defined pH)—complexes which differ markedly in their stability.

The system uranyl ion-Trilon B-stable elements is well-known. Oxalic acid is very useful when determining thorium in the presence of zirconium; the oxalic acid binds the zirconium and has practically no masking effect on the thorium (in a 3–9*N* hydrochloric acid medium). Fluorides, at pH 2, bind thorium almost completely and do not inhibit the colour reaction of uranyl ion with arsenazo III. Other selective masking, complex-forming compounds can, no doubt, be found.

The selectivity can also be increased by utilising the so-called extraction-photometric methods for the determination of elements; these methods have been described in recent publications.[6,7] It has been shown that complexes of arsenazo III and elements can be extracted with butyl or amyl alcohol when salts of a heavy organic cation, *e.g.* diphenylguanidine chloride, are introduced into the solution. In this case direct photometric determination is carried out in the organic phase, without re-extraction. Thus the determination is combined with the simultaneous separation from other, non-extracted elements. The extraction-photometric methods have been investigated for uranium[7] and thorium.[6] They have also been used for zirconium and rare earths but in this case it is preferable to employ more hydrophobic analogues of arsenazo III, *e.g.* tetrabromo-arsenazo III, which is 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-4,6-dibromophenylarsonic acid].

A high degree of selectivity can be achieved by combining these methods for the determination of thorium, zirconium, hafnium, and uranium$^{IV\&VI}$. When analysing substances containing large or average concentrations of the above-named elements it is possible to carry out direct determinations in the solutions obtained after decomposing these substances, without separation of the admixtures. Preliminary concentration is required during the analysis of rock-samples and of other materials containing small amounts of the elements. This is achieved by a one-stage precipitation reaction,[8,9] a single-stage extraction,[7] or similar comparatively simple methods. Complete separation of the admixtures is not necessary—this facilitates the method considerably.

The selectivity is also influenced by a larger or smaller excess of reagent used during the photometric determination. In the latter case, *i.e.* when the reagent is present in not too large a molar excess with regard to the element to be determined (two-to-three-fold), it will be observed that the degree of selectivity is increased.

Complex-formation of arsenazo III *with elements*

Arsenazo III forms 1:1 complexes with 2+ and 3+ charged cations of elements, *e.g.* Sr, UO_2^{2+}, ZrO^{2+} or La. With 4+ charged cations, *e.g.* Th, Zr, Hf, U^{IV}, the composition may be related to the conditions (pH and the ratio of the components) and E:R=1:1 or E:R=1:2. The composition of complexes of 4+ charged elements is always in the ratio 1:2 under the conditions for colour reactions, when the reagent is present in large excess.

The structure of the complex and the reasons for its unusually high stability will

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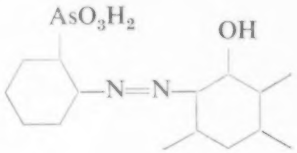
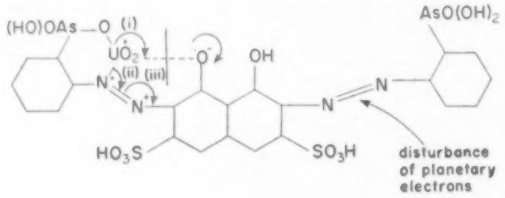
be described in future communications. It should be noted here that although arsenazo III contains two functional groups:



only one of these groups partakes in the complex-formation with elements. The structure of the complex of uranium^{VI} with arsenazo III, for example, can be depicted as follows:



METHODS FOR THE DETERMINATION OF ELEMENTS

Thorium

The method is perhaps most selective for the determination of thorium. Stable elements do not inhibit the reaction if the ratio of thorium to elements is not in excess of: Zr—1:1,000; UO_2^{2+}—1:6; rare earths (Ce-subgroup)—1:50; rare earths (Y-subgroup)—1:100; Ti—1:10; Cr^{III}—1:200; Ni—1:500; Fe^{III}, Pb, Co, Ca, Al and other elements—1:1,000 to 5,000. It was previously pointed out that zirconium can be masked effectively by oxalic acid and that uranium^{IV} readily oxidises to uranium^{VI}. Zirconium is masked most effectively in a 2.5–3.0*N* hydrochloric acid medium. For every 25 ml of the final solution one has to introduce 6 ml of hydrochloric acid (sp. gr. 1.19), 10 ml of 4% oxalic acid solution and 0.5 ml of a 0.1% aqueous solution of arsenazo III during the photometric determinations. The content of thorium should be 1–25 μg.[9] The measurements are carried out with a spectrophotometer at 665 mμ or with a photocolorimeter with a red-light filter. The effect of the acidity on the colour-formation of the thorium arsenazo III complex is shown in Fig. 2.

The methods for the determination of thorium in various substances can be used for the direct determination of thorium as well as for samples with a low thorium-content, after preliminary separation of the admixtures.[3,6,8–10]

The following procedure may be adopted when analysing rock samples:[9]

Decompose 0·1–0·5 g of the sample, containing 0·0001% and higher quantities of thorium, supposedly containing 1–25 μg of thorium, with hydrofluoric acid. Evaporate, treat the residue with hydrofluoric acid and wash with water. After filtering, transfer the precipitate to a platinum dish and treat with perchloric acid + hydrochloric acid. After evaporating, dissolve the residue in 1·6 ml of hydrochloric acid (1:1) + 5 ml of water and transfer to a 25-ml volumetric flask. Add ascorbic acid to reduce the iron^{III} and 10 ml of 4% oxalic acid solution in hydrochloric acid (1:1), 0·5 ml of a 0·1% solution of arsenazo III and dilute to the mark with water. The photometric determination is carried out on a FEK–M with a red-light filter or on a SF–4 at 665 mμ in 50-mm cells. The thorium content is found via a calibration curve. Six to 8 determinations can be carried out in 6 hr.

The determination of thorium is not inhibited by substantial quantities of niobium. Thus it is possible to carry out direct determinations of thorium in niobium concentrates after dissolving the sample, without preliminary separation of niobium.[10] Analysis conditions are essentially identical to those described above.

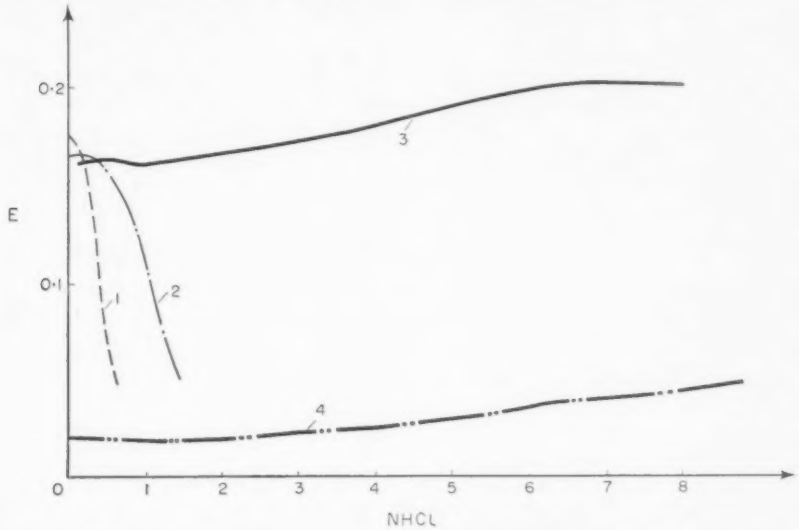


FIG. 2.—Effect of pH on the colour of the thorium complexes with the various reagents:
1. Arsenazo I, conc. Th–1·2 × $10^{-5}M$, 650 mμ;
2. Arsenazo II, conc. Th–1·2 × $10^{-5}M$, 600 mμ;
3. Arsenazo III. conc. Th–0·4 × $10^{-5}M$, 665 mμ;
4. Arsenazo III., concentration of the reagents 0·5 × $10^{-4}M$.

Uranium

The method for the determination of quadrivalent uranium with arsenazo III is considerably more selective than for the determination of uranium^{VI}. Preliminary reduction has to be carried out; this and the stability of uranium^{IV} may cause various difficulties; however, this method of determining uranium appears to be most satisfactory.[11] As in the case of thorium most cations and anions do not inhibit the reaction. Zirconium is masked by oxalic acid and iron^{III} is reduced with ascorbic acid. Only thorium causes substantial interference. The following analysis procedure may be used when the quantities of uranium and thorium are of the same order: up to the time of reduction of uranium only thorium is determined; after completion of the reduction the sum of thorium + uranium^{IV} is determined and the uranium content found from the difference.

The method of determination is as follows:[11]

Decompose 0·5 g of the rock sample, ore cake, *etc.*, containing 0·002% and larger quantities of uranium, by heating with hydrochloric acid + hydrogen peroxide. Dilute with 4*N* hydrochloric acid and filter into a 100-ml volumetric flask. Take two aliquots of 10 ml each and place in small flasks. Add 5–10 mg of ascorbic acid to both fractions (until discoloration of the brown colour of iron^{III} sets in) and to one fraction 5–6 granules of zinc (to reduce the uranium). Run off the solutions into 50-ml volumetric flasks, without transferring the zinc, and rinse out the flasks with 4*N* hydrochloric acid.

To each test sample add 2 ml of 4% oxalic acid solution, 2 ml of a 0·05% solution of arsenazo III and dilute to the mark with 4*N* hydrochloric acid. Photometric measurements are carried out at

665 mμ or on a photocolorimeter with a red-light filter in 20-mm cells, using the non-reduced aliquot as a standard.

The uranium content is found via a calibration curve: small volumes of the solution, containing, respectively 0, 4, 8, 15, 30 and 40 μg of uranium are subjected to the above procedures whilst maintaining accurately the degree of acidity, the period of reduction and other conditions.

The extraction-photometric method[7] can be used to achieve improved selectivity during the determination of sexavalent uranium.

Decompose a few mg of the sample, containing 1–50 μg of uranium, according to the mineralogical composition of the sample. After evaporation, treat the dry residue with 2·0 ml of 0·05*N* hydrochloric acid, 2·5 ml of a 5% solution of Trilon B, 1·00 ml of a 0·05% solution of arsenazo III, 0·5 ml of a 20% solution of diphenylguanidine chloride and add 5·00 ml of butanol. After extraction, transfer part of the upper layer to a 10-mm cell and evaluate photometrically, either on a spectrophotometer at 660 mμ or on a photocolorimeter with a red-light filter.

The uranium content is found via a calibration curve plotted in the manner described above.

Direct photometric determination without separation of the stable elements can be employed when determining uranium in pitchblende or in substances containing traces of admixtures. Sulphates, phosphates and even limited quantities of fluorides do not act as inhibitors. The photometric determination of uranyl ion is carried out at pH 1.5–3.5, and of uranium^{IV} in 3–9*N* hydrochloric acid.

Zirconium

The method is very selective for the determination of zirconium. In most cases, even during the determination of zirconium in complex samples, *e.g.* in ores,[12] and alloys based on copper, aluminium, magnesium and titanium, in the presence of niobium, tantalum and other elements,[13] it is not necessary to separate the stable elements or to concentrate the zirconium. Photometric measurements can be taken immediately after decomposing the sample. The complex of arsenazo III and zirconium is very stable and sulphates, phosphates and other anions have only a slight effect. Oxalates and fluorides mask zirconium. The sensitivity is approximately 0.01–0.05 μg/ml of zirconium (see Table II).

The effect of the acidity and the ratio of zirconium: arsenazo III on the intensity of coloration is shown in Figs. 3 and 4. The determination of zirconium can be carried out in strongly acidic media—from 2 to 11*N* hydrochloric acid *i.e.* under conditions where practically no hydrolysis or partial polymerisation of the zirconium cations occurs. This ensures very accurate results and good reproducibility of the analyses.

Goryushina and Romanova[12] showed that even in such complex samples as tin and titanium concentrates, magnesium fractions obtained on concentrating ores of various origin, *etc.*, direct photometric determination of zirconium can be carried out in solutions obtained after decomposing the substances, without preliminary separation of the stable elements:[12]

Fuse 0·1–0·2 g of the material in a platinum dish with 5 g of a mixture (1:1·5) of borax and sodium carbonate at 900°, for 7 to 10 min. After cooling, add boiling water and decant the liquid, with the residue of hydrates, into a beaker. Dilute the mixture with water to 150 ml and heat to achieve better coagulation. Filter off the residue, wash and dissolve in 2*N* hydrochloric acid. Aliquots containing 5 to 30 μg of zirconium are taken; to these are added 3 ml of a 1% gelatin solution, 1·00 ml of a 0·1% solution of arsenazo III and up to 50·0 ml of 2*N* hydrochloric acid. Photometric measurements are taken with a FEK–M, in a 2·0-cm cell, with a red-light filter. The zirconium-content is found via a calibration curve, plotted under identical conditions.

The concentration of 2*N* hydrochloric acid was selected on considering the most practical working conditions for the analysis of substances containing high or average concentrations of zirconium (0.1% or more of zirconium). When the zirconium-content is low (0.01% and less) determinations should be carried out in 9*N* hydrochloric acid. The only drawback is the relatively high volatility of hydrochloric

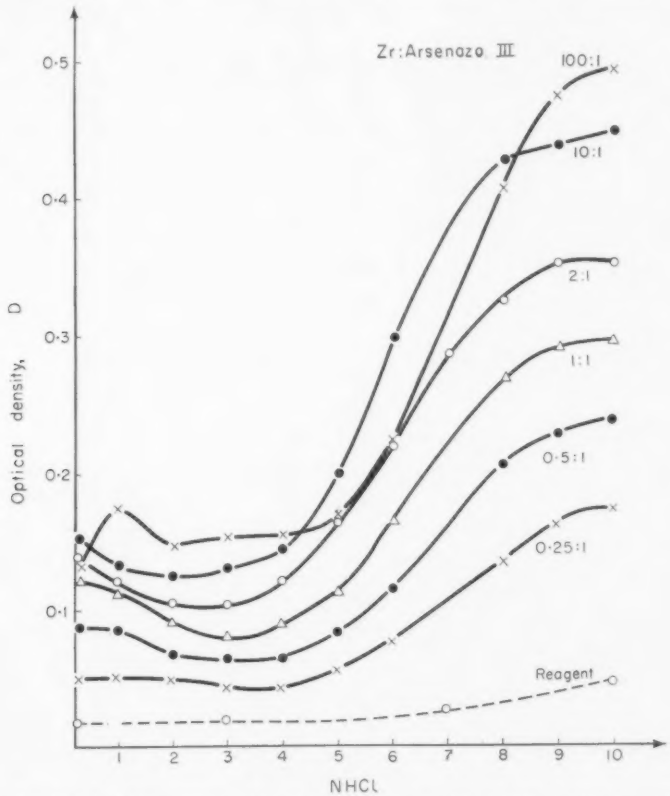


Fig. 3.—Effect of the concentration of hydrochloric acid and of the molar ratio of zirconium: reagent on the colour intensity (Concentration of arsenazo III: $0{\cdot}9 \times 10^{-5}M$, spectrophotometer SF-4, 665 mμ, 10-mm cell).

acid. In some cases it may be more advantageous to work at acidities corresponding to the azeotropic composition of the system—hydrochloric acid 1:1(~6.1*N* hydrochloric acid.[14]

Zirconium must be concentrated when analysing alloys and substances containing zirconium in the form of admixtures (from 0.01% to 0.0001%). Titanium is known to be a very good co-precipitator for zirconium but its use has been proved inadvisable because it causes considerable interference when determining zirconium photometrically with reagents such as pyrocatechol violet, morin, phenylfluorone *etc.* These difficulties do not arise with arsenazo III. Titanium causes no interference even at ratios of zirconium:titanium = 1:1000. The determination of zirconium in aluminium–magnesium alloys is described as an example; it was investigated by Kuznetsov and the present author:

Weighed samples of the alloy (0·2–2 g), supposedly containing 2–40 μg of zirconium, are dissolved in 6*N* hydrochloric acid, to which nitric acid is added—to dissolve the copper.

Evaporate the samples to wet salts* and add 1 ml of a titanium solution containing 5 mg/ml of titanium, 5 ml 6*N* hydrochloric acid, then dilute with water to 50–100 ml.

Add 13 ml of 40% sodium acetate trihydrate solution. Check the acidity with universal indicator paper; the pH should be within the limits 2·0 to 2·5.

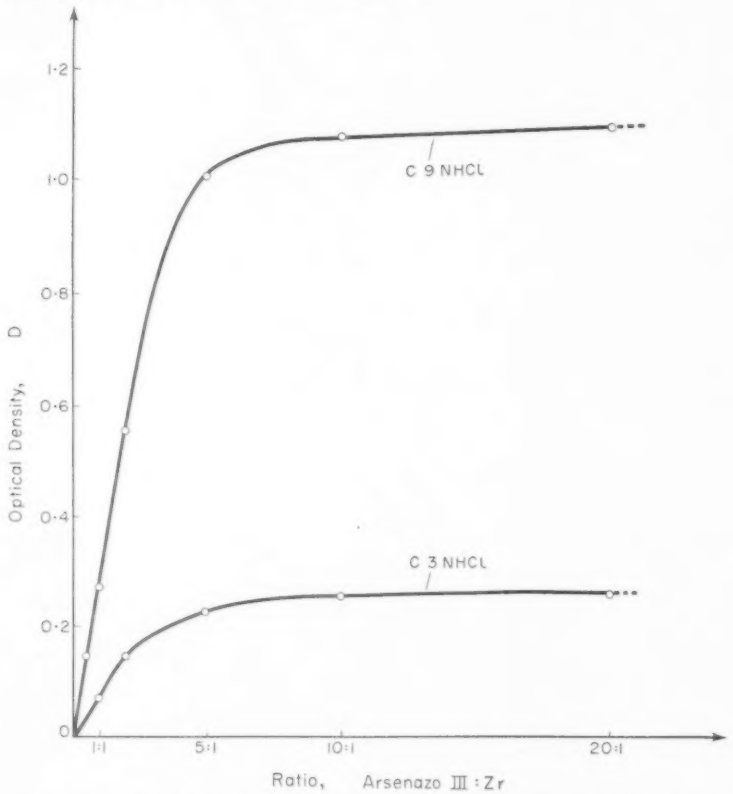


FIG. 4.—Effect of the molar ratio of reagent: zirconium on the colour intensity of the arsenazo III–zirconium complex (Concentration of zirconium: $0{\cdot}9 \times 10^{-5}M$, taken against water).

Maintain on a hot water bath for 30–60 min. The small quantity of flaky precipitate of titanium and zirconium hydroxides is filtered through a 7-cm diameter filter paper and washed with water.

Transfer the filter, together with the residue, into the same beaker in which the precipitation was carried out, add 10 ml of 6*N* hydrochloric acid and heat the mixture for 15–20 min whilst stirring with a small glass rod. A homogeneous paper pulp is formed and the solution is filtered into a 50-ml volumetric flask; the beaker and filter are washed 3 times with small quantities (2·5 to 3 ml) of 6*N* hydrochloric acid. It is necessary to allow the solution to drain off completely after each washing because the volume of 6*N* hydrochloric acid, which can be used for the washing is limited to 9–10 ml.

Add 1·00 ml of an arsenazo III solution, agitate the mixture, then add 30·0 ml of conc. hydrochloric acid (sp. gr. 1·18†) and dilute with 6*N* hydrochloric acid to the mark. Close the flask tightly to avoid losses in hydrochloric acid.

* Evaporation to wet salts is not absolutely necessary. In this case the required pH of the solution is established, after diluting the solution, by using universal indicator paper or an internal indicator *e.g.* methyl violet, adding sodium acetate until the colour changes from blue to dark blue-violet.

† Use 28 ml when the sp. gr. of the conc. hydrochloric acid is 1·19, 32 ml for a sp. gr. of 1·17 and 34 ml for a sp. gr. of 1·16.

Photometric measurements are carried out on a spectrophotometer at 665 mμ, in a 10-mm cell, or on a photocolorimeter with a red-light filter, in a 20-mm cell. The solution of the No. 1 calibration curve is used as standard.

Calibration curve. Introduce into a series of 50-ml volumetric flasks: 0, 0·4, 0·8, 1·6, 4·0, 6·0 and 8·0 ml, respectively, of a zirconium solution in 6*N* hydrochloric acid containing 5 μg/ml of zirconium, a titanium solution in 6*N* hydrochloric acid, containing 5 mg/ml of titanium, 1·0 ml; a 0·25% solution of arsenazo III, 1·00 ml; conc. hydrochloric acid, 30 ml (sp. gr. 1·18); and dilute with 6*N* hydrochloric acid to the mark.

Note. Instead of 6*N* hydrochloric acid, azeotropic hydrochloric acid (~6·1*N* hydrochloric acid) can be used, or a 1:1 solution of hydrochloric acid prepared from the conc. acid. In this case the calibration curve is plotted using the 1:1 acid.

Zirconium and hafnium

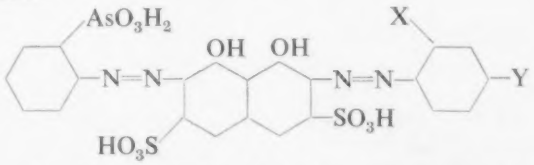
Arsenazo III can also be used for the photometric determination of zirconium and hafnium when both elements are present. The principle of the method has been described earlier and is general for all reagents giving colour reactions with zirconium and hafnium. It is as follows: the sum of zirconium + hafnium is determined photometrically at two pH values at which superposition is observed in the first case and at which, in the second case, the largest discrepancy occurs between the colour intensity of the corresponding zirconium and hafnium complexes.[14] The zirconium and hafnium contents can be calculated from the results obtained.[14] Elinson and Mirzoyan state that the photometric determination of zirconium + hafnium should be carried out in 1*N* and 4*N* hydrochloric acid.

Rare earths

In weakly acidic solutions yttrium, lanthanum and the lanthanides develop a blue-green coloration with arsenazo III. Scandium gives a violet colour. The determination is of a sufficiently high degree of sensitivity: 0.5 μg of the element and larger quantities can be determined in 25 ml of solution. The reaction is not very selective: all elements reacting with arsenazo III act as inhibitors when the pH at which they begin to hydrolyse is lower than the pH of the start of the hydrolysis of the rare earth elements. The following substances do not act as inhibitors in quantities up to 5–50 mg in 25 ml: aluminium, iron, magnesium, sodium, potassium, sulphates, chlorides, phosphates.[15]

Analogues of arsenazo III

Kuznetsov, Dedkov and Savvin[6] succeeded in synthesising completely different analogues of arsenazo III by the azo-addition of arsenazo I and various amines on adding calcium salts:



where $X = H$; $Y = H_3SO_3H$, NH_2 NO_2, $N(CH_3)_2$, $A_SO_3H_2$;
$Y = H$; $X = COOH$, SO_3H, OH, NO_2.

Preliminary analytical tests have proved that these compounds also give colour reactions with many elements, especially with those where arsenazo I and arsenazo III

give colour reactions. The stability of complexes formed by these compounds lies between the stability of the corresponding complexes of arsenazo I and arsenazo III. Further investigations will be carried out on the bis-azo-derivatives of chromotropic acid.

Synthesis of arsenazo III

The synthesis is quite simple and easily reproducible.

The compound is prepared by the azo-addition of concentrated solutions of diazotised *o*-aminophenylarsonic acid and chromotropic acid in a medium of excess calcium hydroxide which is used simultaneously as a base and as an activator.[3]

Dissolve 15 g (0·069 mole) of *o*-aminophenylarsonic acid, whilst heating slightly, in 30 ml of water and 15 ml of conc. hydrochloric acid (sp. gr. 1·18). After cooling, add 50 g of crushed ice. To this mixture add, with constant stirring, a solution of 5 g of sodium nitrite in 10–15 ml of water and a small excess of nitric acid (accurately tested with iodised starch paper) which is subsequently removed with sulphamic acid.

Dissolve 6·5 g (0·0179 mole) of the disodium salt of chromotropic acid in 20 ml of water and introduce a mixture of 10 g of calcium oxide and 30 ml of water into the solution. Add 50 g of crushed ice as well as the previously prepared diazonium solution, under constant agitation. The solution turns a blue–violet colour. Allow to stand for 30 min to 2 hr at room temperature.

Carry out tests to ascertain the termination of the azo-addition reaction. Add 1 drop of the reaction mixture (*ca.* 0·03 ml) to 50–100 ml of water. Place 5–10 ml of the resulting blue solution in a test tube and to this add 2–3 drops of conc. hydrochloric acid. The solution turns pinkish-crimson. Add 1 drop of thorium salt solution, containing 10–20 mg/ml of thorium, when the solution acquires the intensive emerald-green colour of the thorium-arsenazo III complex. Decant the solution into two test tubes and to one test tube add 10–15 drops (*ca.* 0·5 ml) of conc. sulphuric acid, whilst constantly agitating and cooling the contents of the test tube. The colour of the solution to which conc. sulphuric acid has been added will differ slightly from the colour of the second fraction if complete addition has occurred; it will turn dark green. If, on the other hand, incomplete addition took place, then the fraction containing sulphuric acid will turn red-violet, crimson or acquire a muddy colour; in this case a mixture of arsenazo I and arsenazo III has been obtained. This may be caused by inadequate purity of the starting materials, *i.e.* of the chromotropic acid and especially of *o*-aminophenylarsonic acid.

Add 1 litre of hot water and 100 ml of conc. hydrochloric acid to the mixture obtained by the addition reaction. Agitate the mixture to dissolve the calcium salts completely, and filter after allowing to settle. Wash the almost black residue with 50–100 ml of hydrochloric acid (1:10) and discard the filtrate. Dissolve the crude product in 1 litre of hot water + 50 ml of 40% sodium hydroxide solution, freed from mechanical admixtures by filtration, acidify with 100 ml of conc. hydrochloric acid and allow to stand for a few hr or overnight. Filter off the precipitate, centrifuge and wash it first with 30–50 ml of water, then with 30–50 ml of ethanol. The last fractions of the filtrate should be free from reaction by-products, *i.e.* from arsenazo I and decomposition products of the excess diazonium compound of *o*-aminophenylarsonic acid. This is tested by the above described qualitative reaction with thorium salts. The yield of arsenazo III is 11–12 g.

Zusammenfassung—Das Reagens Arsenazo III (1,8-dioxynaphthalin-3,6-disulfonsäure-2,7-bis [azo-2-phenylarsinsäure]) gibt Farbreaktionen mit einer Reihe von Elementen. Anionen beeinflussen die Färbungen nur zu einem geringen Grade und es ist möglich bei niederen pH-Werten zu arbeiten. Die Reaktion ist sehr sensitiv und kann zur photmetrischen Bestimmung von Th, Zr, Hf, U und einiger, anderer Metalle herangezogen werden. Th, Zr und U zeigen die höchste Empfindlichkeit. Material, welches diese Elemente enthält, kann direkt nach Auflösen der Probe und ohne weitere Abtrennungen zur Analyse herangezogen werden.

Résumé—Le réactif arsénazo III (1,8-dihydroxynaphtalène-3,6-disulfonique acide-2,7-bis[azo-2-phénylarsonique acide]) donne des réactions colorées avec un certain nombre d'éléments. Les anions n'influent que très peu sur les réactions, et il est possible de travailler à de faibles valeurs de pH. La

réaction est très sensible, le composé peut ensuite être utilisé pour le dosage photométrique de Th, Zr, Hf, U et d'autres éléments. La méthode est la plus sélective pour Th, Zr et U(IV). Les matériaux contenant ces éléments peuvent être analysés directement, dans des solutions formées après dissolution des échantillons, sans séparation des éléments.

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SHORT COMMUNICATION

Chelatometric determination of caesium

(*Received* 5 *May* 1961. *Accepted* 15 *May* 1961)

INTRODUCTION

CAESIUM salts must be carefully dried and dehydrated before being weighed. These operations require special care and several hours may elapse before constant weight is attained. On the other hand, caesium salts, being much more volatile than the corresponding sodium salts, may suffer a partial volatilisation through rapid or prolonged heating, especially when minute quantities of caesium perchlorate are treated.

These difficulties suggested to the author the advisability of using a titrimetric procedure for the determination of caesium, utilising the perchlorate precipitate obtained by the classical technique. The literature on chelatometric titrations does not mention any method, direct or indirect, for the determination of caesium.

The principle of the present method is based on the transformation of the perchlorate to caesium chloride[1,2] followed by precipitation of the chloride with silver nitrate. The chelatometric procedure for the titration of silver[3,4] is applied. This is based on the nickel that is liberated when the silver salt is treated with potassium nickelicyanide:

$$2AgCl + [Ni(CN)_4]^{2-} \rightarrow 2[Ag(CN)_2]^- + Ni^{2+} + 2Cl^-$$

The liberated nickel is titrated with EDTA, using murexide to indicate the end-point.

EXPERIMENTAL

Reagents

Ammonium chloride: AnalaR.
Silver nitrate: 5% and 0·1% aqueous solutions.
Nitric acid: Concentrated, and 1% aqueous.
EDTA: 0·1*M* (or, if necessary, 0·01*M*).
Murexide: Saturated aqueous solution.
Potassium nickelicyanide: 0·1*M*. Titrate 0·1 mole of $NiSO_4$ in 500 ml of water, made ammoniacal, with 1*M* KCN until murexide changes from yellow to purple. Dilute the solution to 1 litre.

Procedure

The caesium perchlorate precipitate is dried rapidly by washing it with a little ether, and it is then removed carefully from the Gooch filter* and introduced into a platinum dish. Two to three g of ammonium chloride are added and mixed intimately with the precipitate. The mixture is covered with a layer of ammonium chloride and heated gently for 1–2 hr, the dish being covered with a watch glass. If a porcelain dish is used, 1 ml of chloroplatinic acid is added to catalyse the reaction.

The temperature should be kept below the melting point of the residual chloride (otherwise the platinum dish may be damaged). More ammonium chloride is added and the mixture is heated for another 0·5 hr. The contents of the dish are cooled and then dissolved in water in a beaker. A few drops of concentrated nitric acid are added and afterwards an excess of 5% silver nitrate solution. The contents of the beaker are boiled for 5 min, the beaker being covered with a watch glass.

When cold, the contents of the beaker are filtered through a Gooch filter. The precipitate is washed twice with 0·1% silver nitrate solution and then twice with 1% nitric acid. The filter and precipitate are introduced into a beaker containing ammoniacal potassium nickel tetracyanide

* If a very small quantity of caesium is analysed, the $CsClO_4$ precipitation is better carried out in a centrifuge tube.

solution. The beaker is warmed gently until dissolution of the precipitate is complete. A few drops of murexide solution are added and the solution is titrated with 0·1*M* EDTA to a yellow to purple end-point.

0·1*M* EDTA solution, *ml* × 26·582 = Cs, *mg*
0·1*M* EDTA solution, *ml* × 28·182 = Cs_2O, *mg*

RESULTS AND DISCUSSION

The results obtained by the above method are very satisfactory. Some results with a solution of caesium carbonate are reproduced in Table I. The analytical reagent was dried at 110° for 4 hr and 5·7805 g were dissolved in 1000 ml of twice distilled water. One ml of this solution is equivalent to 5 mg of Cs_2O. The caesium carbonate was transformed into caesium perchlorate and was then treated by the method described. Titrations 1–5 were carried out with 0·01*M* EDTA and titrations 6–10 with 0·1*M* EDTA.

TABLE I.

No.	Cs_2O taken, *mg*	Cs_2O found, *mg*	Difference, *mg*	Difference, %
1	5·0	5·1	+0·1	+2·0
2	10·0	9·9	−0·1	−1·0
3	15·0	15·1	+0·1	+0·7
4	20·0	19·8	−0·2	−1·0
5	30·0	30·1	+0·1	+0·3
6	40·0	40·2	+0·2	+0·5
7	50·0	50·3	+0·3	+0·6
8	75·0	74·7	−0·3	−0·4
9	100·0	100·5	+0·5	+0·5
10	200·0	201·6	+1·6	+0·8

Laboratory of Analytical Chemistry ARTHUR DE SOUSA*
Faculty of Science
University of Lisbon, Portugal

Summary—An indirect chelatometric method for the determination of caesium is described. Caesium is precipitated as perchlorate according to the classical procedure and the precipitate is heated with ammonium chloride to reduce the perchlorate to chloride. Caesium chloride is dissolved in water and the chloride is precipitated as silver chloride. This precipitate is dissolved in an ammoniacal solution of potassium nickelicyanide. Silver displaces nickel in the complex and the freed nickel is titrated with EDTA. Caesium is obtained indirectly by multiplying the quantity of EDTA solution by a factor. The results are very satisfactory and the method is as rapid as the gravimetric procedure, with the advantage of avoiding the tedious drying and weighing of the perchlorate precipitate.

Zusammenfassung—Eine indirekte, chelatometrische Methode zur Bestimmung von Cäsium wird beschrieben. Cäsium wird als Perchlorat gefällt und durch Erhitzen des Niederschlages mit Ammoniumchloride zu Cäsiumchlorid reduziert. Letzteres wird in Wasser gelöst, Chlorid mit Silber gefällt und das Silberchlorid mit Nickeltetracyanid umgesetzt. Das in Freiheit gesetzte Nickelwird chelometrisch bestimmt. Die Methode gibt sehr gute Resultate und vermeidet das zeitraubende Trocknen und Wägen des Niederschlages.

Résumé—L'auteur décrit une méthode complexométrique indirecte de dosage du caesium. Le caesium est précipité sous forme de perchlorate suivant le procédé classique; le précipité est chauffé avec du chlorure d'ammonium pour réduire le perchlorate en chlorure. Le chlorure de caesium est dissous dans l'eau, et le chlorure est précipité à l'état de chlorure d'argent. Ce précipité est dissous dans une solution ammoniacale de nickelocyanure de potassium. L'argent déplace le nickel de son

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complexe, et le nickel libre est titré par complexométrie. La quantité de caesium est obtenue indirectement en multipliant la quantité de solution d'EDTA utilisée par un facteur. Les résultats sont très satisfaisants, et la méthode est aussi rapide que la gravimétrie, elle a de plus l'avantage d'éviter le séchage pénible et la pesée du précipité de perchlorate.

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NOTICES

Material for this section should be sent directly to the Assistant Editor

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DEUTSCHLAND

Dienstag–Freitag 10–13 *April* 1962: **Erstes Europäisches Symposium "Zerkleinern"**, 36. Veranstaltung der Europäischen Föderation für Chemie-Ingenieur-Wesen: vorbereitet und durchgeführt von *der Verfahrentechnischen Gesellschaft (VTG) im Verein Deutscher Ingenieure* und *der DECHEMA Deutsche Gesellschaft für chemisches Apparatewesen, Frankfurt (Main)*. Frankfurt (Main), Deutschland.

Drei Themengruppen werden behandelt, und zwar: Gruppe (A) Physikalische und theoretische Grundlagen des Zerkleinerns Gruppe (B) Grundlagen und neuere Entwicklungen der Zerkleinerungsmaschinen

Gruppe (C) Anwendungstechnik, Zerkleinerung bestimmter Stoffe.

Sekretariat: Verfahrenstechnische Gesellschaft
Frankfurt (Main) 7, Rheingau-Allee 25.

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FRANCE

Lundi–Mardi 9–10 *Octobre* 1961: **Commission Internationale d' Analyses;** *Comite International de la Detergence. Paris.*

ITALY

Thursday–Friday 9–10 *November* 1961: **Scientific and Technical Documentation and Information in Chemistry:** Under the auspices of *I.U.P.A.C.* and *Federation of Scientific and Technical Associations of Milan* and organised by *Lombard Section of Italian Chemical Society, Italian Society of Pharmaceutical Sciences* and *Italian Association of Chemical Engineering* with co-operation of *Centre Français d'Exchanges et de Documenation Technique*. House of the Scientific and Technical Associations, 10, Via del Politechnico, Milan.

The programme has been provisionally arranged to cover:

1. Publication of documents.
2. Organisms of documentation and information.
3. Current and retrospective bibliographies.
4. Automation in the research for information.

POLAND

Thursday–Friday 28–29 *September* 1961: **Symposium on Gas Chromatography:** *Section of Gas Analysis of Analytical Committee of Polish Academy of Sciences* and the *Chief Technical Organisation*. Kraków.

The programme will include a number of general lectures and scientific communications given by Polish, Czechoslovakian and German Democratic Republic participants. Some lectures by manufacturers of apparatus (Pye, Siemens) are also expected.

SWITZERLAND

September 1963: **Second Congress of International Federation of Automatic Control:** On the invitation of *Swiss Association for Automatic Control*. Basle.

Nearly all papers should deal with theory or with applications of automatic control. A few papers will be adopted on components of control devices and on general items. Papers should deal with one of the following problems:

1. Theory

(a) Discrete Systems
(b) Stochastic Systems
(c) Optimal Systems
(d) Learning Systems
(e) Systems Reliabilty

2. Applications

(a) Process Dynamics
(b) Computer Studies of Applications, on or off line
(c) Optimising or Adaptive Control Applications

3. Components

(a) New and Effective Devices
(b) Measurement of the Reliability of Components

Papers may be submitted in English, French, German or Russian.

Enquiries should be addressed to Secretary of I.F.A.C., Dr.-Ing. G. RUPPEL, Prinz-Georg-Strasse 79, Düsseldorf, Germany.

UNITED KINGDOM

National Lending Library for Science and Technology of D.S.I.R. has recently published a list of Irregular Serials received from U.S.S.R. and Bulgaria. The main part of the list is arranged in alphabetical order of the title using the cyrillic alphabet. Following the main list, there is a short list of serials received from Latvia, Lithuania and Estonia and published in the roman alphabet, A list of books received from U.S.S.R. has also recently been established.

Listed items may be borrowed from National Lending Library of D.S.I.R., Boston Spa, Yorkshire.

Tuesday–Friday 18–21 *September* 1962: **First International Congress of Food Science and Technology.** Imperial College of Science and Technology, London.

The programme is divided into four sections, which will run concurrently throughout the four days of the Congress except for a number of periods devoted to Plenary Sessions and Congress Symposia:

Section A. Chemical and Physical Aspects of Foods.
Section B. Biological and Microbiological Aspects of Foods.
Section C. Quality, Analysis and Composition of Foods.
Section D. Manufacture and Distribution of Foods.

The following sub-sections are envisaged to Section C:

1. Specialised analytical techniques.
2. Detection and determination of minor constituents.
3. Application of automation to analysis and quality control.

Further details and registration forms may be obtained from Mr. F. J. GRIFFEN, 14, Belgrave Square, London, S.W.I.

UNITED STATES OF AMERICA

Sunday–Thursday 1–5 *October* 1961: **Fall Meeting:** *Electrochemical Society*. Statler Hilton Hotel, Detroit, Mich.

Monday–Thursday 9–12 *October* 1961: **Eleventh Annual Instrument Symposium and Research Equipment Exhibit:** *Washington Sections of American Chemical Society, Instrument Society of America, American Association of Clinical Chemists, Society of American Bacteriologists, Society for Applied Spectroscopy* and *Society for Experimental Biology and Medicine*. National Institutes of Health, Bethesda, Md.

Monday–Wednesday 16–18 *October* 1961: **Ninth Detroit Anachem Conference:** *Association of Analytical Chemists*. Wayne State University.

Monday–Thursday 16–19 *October* 1961: **Second International Vacuum Congress:** *International Organisation for Vacuum Science and Technology* and *American Vacuum Society*. Sheraton Park Hotel, Washington, D.C.

Friday 20 *October* 1961: **Fifth Annual Symposium on Advances in Tracer Methodology:** *New England Nuclear Corporation*. Shoreham Hotel, Washington, D.C.

Wednesday–Friday 15–17 *November* 1961: **1961 Eastern Analytical Symposium and Instrument Exhibit:** *Analytical Groups of New York and North Jersey Sections of American Chemical Society, New York, Delaware Valley, New England and Baltimore-Washington Sections of Society for Applied Spectroscopy* and *Metropolitan Microchemical Society*. Statler Hilton Hotel, New York City.

The meeting will consist of a series of 3-hour symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities.

The programme headings are as follows:

Wednesday 15 *November*

Detectors for Gas Analysis.
X-Ray Spectroscopy.
Storage and Retrieval of Infrared Spectral Data.
Gas Chromatography with High Molecular Weight Organic compounds.
Nuclear Magnetic Resonance.
Emission Spectroscopy.

Thursday 16 *November*

Mass Spectroscopy.
Electroanalytical Methods.
Automation in Microchemical Analysis—Panel Discussion.
Advances in Instrumentation: Infrared Spectroscopy Clinic.
Advances in Biochemical Analysis.
Electroanalytical Methods.
New Developments in Instrumental Techniques for Molecular Weight Determinations.
Advances in Instrumentation:
(a) Emission Spectroscopy Clinic
(b) X-Ray Spectroscopy Clinic.

Friday 17 *November*

Food Additive Analysis.
Applications of Radioistopes.
Advances in Physical and Chemical Separations.
Applications of Nuclear Activation Analysis.
Advances in Physical and Chemical Separations.

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PAPERS RECEIVED

A spot test for uranium^{VI} with resacetophenone-oxime: C. RAMA RAO. (6 *June* 1961).

Spectrophotometric studies on technetium and rhenium: M. AL-KAYSSI, R. J. MAGEE and C. L. WILSON. (27 *June* 1961).

New redox systems-IV: Oxidation of cobalt^{II} with iron^{III} salts in 2:2 bipyridyl solutions. FRANTISEK VYDRA and RUDOLF PŘIBIL. (27 *June* 1961).

A pH-metric study of some bivalent metal sulphosalicylates: V. S. K. NAIR. (29 *June* 1961).

The photometric determination of scandium by means of α-(2, 4-dioxyphenylazo)-pyridine: A. I. BUSEV. (3 *July* 1961).

Contribution to the basic problems of complexometry-IX: Thioglycollic acid as masking agent RUDOLF PŘIBIL and VLADIMIR VESELY. (3 *July* 1961).

A qualitative test for detection of ferrocenes: J. D. BEHUN. (10 *July* 1961).

A comparative study of some lanthanon chelates of alizarin complexan as reagents for fluoride: R. BELCHER and T. S. WEST. (10 *July* 1961).

A study of the cerium^{III} alizarin complexan-fluoride reaction: R. BELCHER and T. S. WEST. (10 *July* 1961).

Thermogravimetric analysis of potassium hydrogen phthalate: A. E. NEWKIRK and RENETTE LAWARE. (17 *July* 1961).

Radiochemical separation of indium by amalgam exchange: R. R. RUCH, J. R. DEVOE and W. W. MEINKE. (18 *July* 1961).

Infrared correlations in the bile acid series: SAMUEL J. LEVIN and CHARLES G. JOHNSTON. (17 *July* 1961).

Steric effect of ortho-substituted alkyl groups on chromatographic absorption of aniline: JACK K. CARLTON and FLOYD B. O'NEAL. (17 *July* 1961).

Activation analysis of molybdenun in plant material: B. VAN ZANTEN, D. DECAT and G. LELIAERT. (19 *July* 1961).

A scheme for the rapid analysis of uranium-ore acid leach solutions: LYN JARMAN and M. MATIC. (20 *July* 1961).

Potentiometric acid-base titration in acetone-water solutions of nitrocellulose: L. R. LEAKE and G. F. REYNOLDS. (1 *August* 1961).

Photometric titrations-V: A selective chelometric determination of cobalt: H. FLASCHKA and J. GANCHOFF. (1 *August* 1961).

Emission spectra from high-frequency excitation-II: The spectra of nitrogen, hydrogen, ammonia: C. L. CHAKRIBARTI, R. J. MAGEE and C. L. WILSON. (1 *August* 1961).

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LETTER TO THE EDITOR

The solubility of bis-8-quinolinolo-zinc*

SIR:

As part of an investigation of factors influencing the intrinsic solubility of chelates, the solubility of several metal 8-quinolinolates have been studied. At this time we would like to communicate the results of our study of the solubility of bis-8-quinolinolo-zinc at 25° and an ionic strength 0·1 molar. The results provide evidence for the existence of $Zn(Ox)_3^-$, a species not considered in previous studies.[1]

In order to minimise the importance of reactions of zinc with other bases, the solubility measurements were made in 8-quinolinol solutions in the absence of foreign buffers in the interval pH 3·1 to 4·1. Over the range pH 3·9 to 9·9, the solutions were saturated with respect to 8-quinolinol, with buffers present in several instances. In this way, the conditions under which the solubility of bis-8-quinolinolo-zinc was determined were different from those reported recently.[1]

The chelate was prepared from an acetic acid solution of ^{65}Zn and zinc perchlorate in the manner described[2] to yield crystals whose powder pattern was identical with that of powdered single dihydrate crystals of bis-8-quinolinolo-zinc. Samples of solution were removed from a solubility apparatus which contained a stirred solvent chelate mixture at 24-hr intervals until equilibrium was attained. The results appear in Table I.

TABLE I.—SOLUBILITY OF BIS-8-QUINOLINOLO-ZINC

pH	pOx	pS
3·12	10·41	2·69
3·16	10·24	2·98
3·40	9·79	3·74
3·59	9·56	4·16
3·74	9·22	4·63
3·90	8·91	5·25
4·14	8·40	6·01
†3·94	8·08	6·56
†4·59	7·43	7·24
†5·62	6·40	7·45
†6·82	5·20	7·46
†7·12	4·90	7·21
†8·73	3·30	6·41
†9·39	2·66	5·62
†9·94	2·14	5·35

† Saturated with 8-quinolinol.

From values reported for the acid dissociation constants[3,4] and intrinsic solubility[5] of 8-quinolinol under the same conditions of temperature and ionic strength, the concentration of the 8-quinolinol anion, $[Ox^-]$, may readily be calculated for each hydrogen ion concentration which prevailed in solution. The values were plotted as the negative logarithm of the 8-quinolinol anion concentration, pOx, against the negative logarithm of the zinc solubility, pS. Proceeding from the lowest 8-quinolinol anion concentration, the solubility of zinc appeared to decrease continuously, pass through a minimum, and increase continuously.

* Presented in part to the 138th meeting of the American Chemical Society in New York, N. Y., September 11 to 16, 1960.

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The values were treated according to the graphical methods described by Sillén.[5] On the acid side of the solubility minimum, the experimental points were compared to normalised curves of the type

$$f(a) = c_0 + c_1 a + c_2 a^2$$

and on the basic side to

$$f(a) = c_0 + c_3/a$$

where

$$f(a) = S, \quad c_0 = \beta_2 K_{so}, \quad c_1 = k_1 K_{so}, \quad c_2 = K_{so}, \quad c_3 = \beta_3 K_{so},$$

and

$$a = 1/[\mathrm{Ox}^-].$$

This procedure will be most successful for the case, $k_3 \ll k_2$.

The values obtained were $\log K_{so} = -23{\cdot}34$, $\log k_1 = 8{\cdot}52$, $\log k_2 = 7{\cdot}32$, $\log k_3 = 4{\cdot}32$. These constants may be compared with values of the solubility product, $\log K_{so} = -23{\cdot}73$, and the first formation constant, $\log k_1 = 8{\cdot}12$, reported previously for an ionic strength of 0·1 *M* and 20°.[6] Although k_3 corresponds to the formation of the species $Zn(Ox)_3^-$, the solubility measurements do not preclude the formation of species of the type $Zn(Ox_2OH)^-$ in the region of increasing zinc solubility. In this connection, it is of interest to note that the stabilities of chelates with 8-quinolinol and 8-quinolinol-5-sulphonic acid are nearly the same.[7] Potentiometric measurements[8,9] have indicated that nickel^{II}, for example, exhibited its maximum co-ordination number toward 8-quinolinol-5-sulphonic acid and 2-methyl-8-quinolinol-5-sulphonic acid. However, reliable measurements could not be made in the region in which the addition of a third 5-sulphonic acid derivative to zinc would occur as predicted from the solubility measurements.

The peculiarly large solubilities observed by Merritt and Weber probably reflect the formation of zinc species that would occur in the absence of a sufficient excess of reagent. Early in our investigation we encountered similar difficulties. A more detailed report will be published later.

Acknowledgment—The authors gratefully acknowledge the financial assistance of the U.S. Atomic Energy Commission in this work.

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11 *May* 1961

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LATE NOTICES

JAPAN

Monday–Saturday 25–30 *September* 1961: **International Conference on Magnetism and Crystallography including Symposium on Electron and Neutron Diffraction:** *International Union of Pure and Applied Chemistry and International Union of Crystallography.* Kyoto, Japan.

UNITED KINGDOM

Thursday–Friday 5–6 *October* 1961: A series of papers on **Selected Topics originating from Analytical Requirements in the Field of Nuclear Technology:** *Society for Analytical Chemistry.* Institution of Mechanical Engineers, Birdcage Walk, London, S.W.1.

Tuesday 10 *October* 1961: **Research Work in Analytical Chemistry at the Technical University of Budapest:** Professor L. ERDEY: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Birmingham and Midlands Section:* Joint Meeting. University, Edgbaston, Birmingham, 15. 7.00 p.m.

Wednesday 25 *October* 1961: **Some Special Problems in the Polarography of Indium and Tellurium:** Professor Dr. M. VON STACKELBERG: *Polarographic Society.* School of Pharmacy, 29–39, Brunswick Square, London, W.C.1. 2.45 p.m.

Thursday 26th *October* 1961: **Aquametry:** Dr. J. H. THOMPSON: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham, 7.00 p.m.

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Wednesday–Saturday 28–31 *March* 1962: **Third Symposium on Spectroscopy:** *Institute of Petroleum, Hydrocarbon Research Group.* William Beveridge Hall, University of London.

The symposium will be similar to those held in 1954 and 1958 and will review progress in many spectroscopic fields. These will include:

Infrared and Raman spectroscopy,

Nuclear and electron-spin resonance,

Vacuum ultraviolet spectra and ionisation potentials,

and X-ray fluorescence and atomic absorption spectra.

Applications for attendance and further details should be sent to The General Secretary, Institute of Petroleum, 61, New Cavendish Street, London, W.1.

Thursday–Friday 27–28 *September* 1962: **Symposium on Techniques of Polymer Science:** *Society for Chemical Industry, Plastics and Polymer Group.*

Papers concerned with novel techniques in polymer synthesis, analysis, including structural analysis, and measurement of physical properties will be featured.

Summaries of proposed contributions should be sent to the Convener of Symposium Subcommittee, 14, Belgrave Square, London, S.W.1, before 1st December, 1961. Complete typescripts of papers provisionally accepted will be called for by 1st June, 1962.

Bureau of Analysed Samples Ltd. has issued the following new British Chemical and Spectrographic Standard Samples:

B.C.S. 300: 6% zinc-aluminium alloy, analysed for Cu, Mn, Si, Mg, Fe, Ti, Cr and Zn.

B.C.S. 304: 10% aluminium bronze, analysed for Cu, Zn, Ni, Fe, Mn, Si and Al.

B.C.S. 305: 75% ferro-silicon, analysed for P, Al, Ca and Si.

B.C.S. 306: 0.4% carbon free-cutting steel, analysed for Si, S, P, Mn and C.

These samples are only available in the finely divided form for chemical analysis.

S.S. 21-24: a series of low tungsten steels analysed for tungsten only, with tungsten contents ranging from 0.7–3.4%.

This series is supplied in the form of 0.75–in. diam. rods, each 3 in. long, for use as spectrographic standards, but is also available in the form of turnings for chemical analysis bearing the reference numbers B.C.S. 281–284.

Further details of these new samples are given in List No. 400R and the latest supplementary insert sheet, which is obtainable free on request from Bureau of Analysed Standards Ltd., Newham Hall, Middlesbrough.

The first of the Society for Analytical Chemistry's Monographs, **Methods for the Analysis of non-soapy Detergent (NSD) Products,** by G. F. LONGMAN and J. HILTON, has recently been published. The Monograph, bound in stout paper covers, uniform in size with *The Analyst*, contains in 30 pages a complete practical scheme for the determination of all components of most non-soapy detergents at present marketed. It is available only from the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1, (*not* through booksellers) at 15s. ($2.00), post free.

A booklet on **Quality Measurement in the Chemical Industry** has recently been published by D.S.I.R.

A physicist and a physical chemist discuss the use of instruments to control processes in the production of chemicals. The authors conclude that all plants should have skilled analysts for measuring product quality, but where successful functioning of a process depends on a large number of routine analytical operations it is worthwhile to consider whether an instrument would be a more effective way of doing the job.

Copies are obtainable free from D.S.I.R. Library, Charles House, 5–11 Regent Street, London, S.W.1.

B.S.I. News announces the following new British Standard: *B.S.* 3397: 1961; *Methods of testing synthetic rubber latices.* This covers method of sampling, and methods for the determination of total solids, coagulum, pH and surface tension. (Price 4s.)

The following revised British standards are also announced:

B.S. 1377: 1961: *Methods of testing soils for civil engineering purposes.* (Price 30s.)

The contents are divided into:

Part 1. General (glossary and list of symbols, apparatus, soil grouping, preparation of samples).
Part 2. Soil classification tests.
Part 3. Soil chemical tests.
Part 4. Soil compaction tests.

B.S. 1747: *Methods for the measurement of air pollution: Part* 1: 1961: *Deposit gauges.* This covers the construction, installation and use of the deposit gauge for the collection and measurement of atmospheric pollution impurities that are deposited by their own weight or with the assistance of rain. The gauge also provides an estimate of the rainfall. A standard report form and a statement of the analytical determinations to be made are included. (Price 5s.)

UNITED STATES OF AMERICA

Thursday–Saturday 28–30 *September* 1961: **Fifth Annual Conference:** *Chemical Division of American Society for Quality Control.* Daniel Boone Hotel, Charleston, W. Va.

Tuesday–Thursday 10–12 *October* 1961: **Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology and Second Conference on Nuclear Chemistry:** *Reactor and Analytical Chemistry Divisions, Oak Ridge National Laboratory.* Civic Auditorium, Gatlinburg, Tennessee. (See also *Talanta*, 1961, **8,** 451).

The programme for the Analytical Chemistry Conference has been arranged under the following headings:

Tuesday 10 *October*
Morning session—Instrumentation
Afternoon session—Spectral Methods of Analysis
Wednesday 11 *October*
Morning session—Burnup and Radiochemical Analysis
Afternoon session—Radiochemical and Activation Analysis
Thursday 12 *October*
Morning session—Analysis of Reactor Materials
Afternoon session—Analysis of Reactor Materials

It is anticipated that the proceedings of the two conferences will be published by the U.S. Atomic Energy Commission.

Enquires concerning the meeting in general and communications relative to the Analytical Chemistry Conference should be addressed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O Box X, Oak Ridge, Tennessee.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—IV

THE CHLORAMINE-T-IODIDE REACTION

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(*Received* 6 *April* 1961. *Accepted* 27 *April* 1961)

Summary—A study has been made of the oxidation by chloramine-T of iodide to free iodine and to monopositive iodine ion over a wide range of conditions. For the oxidation to free iodine, sulphuric or acetic acid media are suitable, and a concentration of 1·0*M* is recommended. Hydrochloric acid is very much less suitable. The reverse titration (the addition of iodide to acidified chloramine-T) is subject to considerable negative errors and is not recommended. Titration in neutral solution, buffered or unbuffered, is impracticable. Bromide to a maximum concentration of 0·01*M* may be present, particularly in sulphuric acid media, without causing error, and arsenic^{III} and iodide in mixture can be successively titrated.

Oxidation to iodine monochloride is quantitative only over the range of hydrochloric acid concentration of 3·0 to 4·0*M*, and is better conducted with carbon tetrachloride as a visual indicator than by the potentiometric method.

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THE status of chloramine-T as a titrimetric reagent has been assessed,[1] methods of standardising reagent solutions have been critically examined,[1] the reaction between chloramine-T and arsenic^{III} has been thoroughly studied,[2] and the performance of a number of indicators in chloramine-T titrimetry has been fully investigated.[3] Next in fundamental importance to the reaction with arsenic^{III} is the reaction of chloramine-T with iodide and iodine. This reaction is basic to (*a*) the standardisation of chloramine-T, both against iodate through thiosulphate and against arsenic^{III} in bicarbonate buffer, (*b*) reactions in buffer media of pH 4–10 in which the presence of iodide is essential before any reaction can occur or the end-point be located, iodine being either a reaction intermediate or purely a catalyst, (*c*) reactions wherein an aliquot of chloramine-T is used to liberate a known quantity of free iodine which is then used in the determination, and (*d*) Andrews-type reactions in which iodine monochloride is used as a reaction intermediate in strong hydrochloric acid solutions, and which depend essentially on the oxidation of iodide or iodine to monopositive iodine ion.

It is necessary, therefore, to establish the quantitativeness of the oxidation by chloramine-T of iodide to free iodine and to iodine monochloride before assessing the validity of determinations involving these reactions. A wide range of conditions has therefore been examined.

Previous work is neither extensive nor very informative. Iodide has been titrated potentiometrically in hydrochloric[4,5] and in sulphuric acid[5] to iodine, and Tomicek and Suchanla[4] report a suitable hydrochloric acid concentration to be 0·35*M*. No sulphuric acid concentration has been specified, though Afanas'ev[6] reported that the reverse titration was satisfactory in 0·5*M* sulphuric acid, with which we are not in entire agreement. Iodide has also been titrated[7] in "dilute" hydrochloric acid in the presence of cyanide to iodine monocyanide using starch as indicator, and in "strong" hydrochloric acid to iodine monochloride using carbon tetrachloride as indicator.

* Present address: Westinghouse Electric Corporation, Semiconductor Division, Youngwood, Pa., U.S.A.

In an earlier paper[1] it was shown that in using chloramine-T to liberate a known amount of iodine, certain minimal requirements in the amount of both acid and iodide employed must be met. In the absence of an excess of free acid, buffer solutions are essential to prevent the pH running so high that the oxidation of iodide ceases, hypoiodite is formed, and both iodine and hypoiodite oxidise thiosulphate to sulphate giving early end-points. At the same time, it was pointed out that although chloramine-T in hydrochloric acid media, with or without the addition of bromide, could oxidise thiosulphate to sulphate, the reaction was not quantitative, suffered from the incidence of side reactions including the formation of tetrathionate, and was not analytically useful. Claims to the contrary have been made[8] and renewed,[9] but the figures adduced in support[9] are in reasonable agreement with our own, *i.e.*, that the reaction shows a deficiency of about 2% from strict stoichiometry. Although the reproducibility is fair, and the eight-fold multiplication of equivalence may be considered as an eight-fold division of the error, we do not find cause to alter our statement because the stoichiometry and precision do not fall within the limit of $\pm 0{\cdot}04\%$ of the oxidation to tetrathionate under the proper conditions.

EXPERIMENTAL

Apparatus and reagents

These have mostly been described before,[1–3] additional reagents being specified below.

Potassium iodide solution, 0·1*M*: Prepared by direct weighing of AnalaR potassium iodide dried for 2 hr at 150° and solution in de-oxygenated water. The solution was standardised by titration in 4·0*M* hydrochloric acid with primary standard potassium iodate,[1] using the potentiometric method and the visual indicators amaranth and carbon tetrachloride to locate the end-point. The results for the factor of the iodide solution were: potentiometric 0·994; amaranth 0·9943, 0·9943; carbon tetrachloride 0·994, 0·994.

Carbon tetrachloride: AnalaR.

Procedure

The concentrations specified are referred to the equivalence point volume of the titration solution, which was arranged to be 200 ml. Andrews titrations with visual indicators were conducted in titration bottles. Before the addition of the iodide solution, all solutions were freed from oxygen by the passage of a rapid stream of carbon dioxide from Drikold for 20 min, and wash water was similarly treated before use. The titration procedure has already been outlined.[1,2] The results shown in the table for potentiometric titrations refer to the particular curves shown in the figures, but replicate determinations were actually made and found to agree within the experimental error in each case.

RESULTS AND DISCUSSION

1. *Oxidation of iodide to free iodine*

The colour of free iodine precludes the use of visual indicators, and the potentials attained are not sufficiently high to permit the use of chemiluminescent indicators such as siloxene, so electrometric methods must perforce be used to locate the end-point. A straightforward classical potentiometric study has been made, using media which had been de-oxygenated by the passage of carbon dioxide in order to avoid direct or induced oxidation of iodide by molecular oxygen. Passage of carbon dioxide was continued during the titration: any loss of iodine by volatilisation is unimportant—indeed it is an advantage, though this could be fully realised only by complete removal of the iodine.

(a) *Direct titration in acid medium.* Titration in sulphuric acid at concentrations between 0·05*M* and 2·0*M* and in acetic acid between 1·0*M* and 2·0*M* gives excellent

results as shown in Fig. 1 and Table 1. A concentration of 1·0*M* for either acid is recommended. Hydrochloric acid is much less satisfactory at a concentration of 0·1*M* to 0·5*M*, while in 1·0*M* acid the potential rise through the end-point is considerably diminished by the partial setting up of the iodine/iodine monochloride redox system,

TABLE I. TITRATION OF IODIDE AT A CONCENTRATION OF 0·01*M* WITH 0·05*M* CHLORAMINE-T UNDER VARIOUS CONDITIONS

Fig.	Curve	Acid	Concn., *M*	Titre, *ml*		Error	
				Calc.	Found	*ml*	%
Direct titration in acid solution:							
1	1	Hydrochloric	0·1	19·98	20·00	+0·02	+0·1
	2		0·5		20·00	+0·02	+0·1
	3		1·0		20·00	+0·02	+0·1
	4	Sulphuric	0·05	19·98	20·01	+0·03	+0·15
	5		0·5		20·01	+0·03	+0·15
	6		1·0		20·005	+0·025	+0·1
	7		2·0		20·00	+0·02	+0·1
	8	Acetic	1·0	19·98	20·00	+0·02	+0·1
	9		2·0		20·01	+0·03	+0·15
Direct titration in acid solution in the presence of 0·01*M* bromide (no distinct inflection in 0·1*M* bromide):							
2	1	Sulphuric	0·5	19·98	20·00	+0·02	+0·1
	2	Hydrochloric	0·25		20·00	+0·02	+0·1
Direct titration in acid solution in the presence of 0·00125 mole of arsenic^{III}:							
2	5	Sulphuric	1·0	45·18	45·16	−0·02	−0·05
	6	Hydrochloric	1·0		45·20	+0·02	+0·05
Reverse titration in acid solution:							
2	7	Sulphuric	0·5	20·02	19·91	−0·11	−0·55
	8		1·0		19·91	−0·11	−0·55
Direct titration to ICl, potentiometric:							
3	1	Hydrochloric	1·0	39·94	39·85	−0·09	−0·23
	2		2·0		39·88	−0·06	−0·15
	3		3·0		39·91	−0·03	−0·08
	4		4·0		39·95	+0·01	+0·03
	5		5·0		40·08	+0·14	+0·35
Direct titration to ICl, carbon tetrachloride as indicator:							
—	—	Hydrochloric	1·0	39·94	39·90	−0·04	−0·1
			2·0		39·91	−0·03	−0·08
			3·0		39·92	−0·02	−0·05
			4·0		39·93	−0·01	−0·03
			5·0		39·93	−0·01	−0·03

and the end-point becomes difficult to locate. No such effect can occur in sulphuric or acetic acids and the potential rise through the end-point is consequently very much greater and sharper. Attempts to increase the size of the potential break at the end-point by removing iodine from solution by extraction into a globule of carbon tetrachloride added to the titration solution[10] met with limited success. Equilibration of potentials was rapid in all cases.

(b) *Direct titration in unbuffered and buffered neutral solution.* In view of instructions[11] and recommendations[12,13] to use chloramine-T as a titrant in "neutral"

unbuffered solutions in conflict with the present findings that chloramine-T is inactive in the absence of added halide,[1,2] that at pH values above 4 the reaction is dependent on the presence specifically of iodide[2] and that arsenic^{III} cannot be titrated in neutral unbuffered media whether iodide be present or not,[1] an investigation was made of the behaviour of chloramine-T under such conditions. If the reagent is capable of reaction in these circumstances, then it should certainly oxidise iodide. The matter is additionally important in respect to reactions of chloramine-T in the presence of iodide of appropriate concentration in media of pH values up to 10.[2]

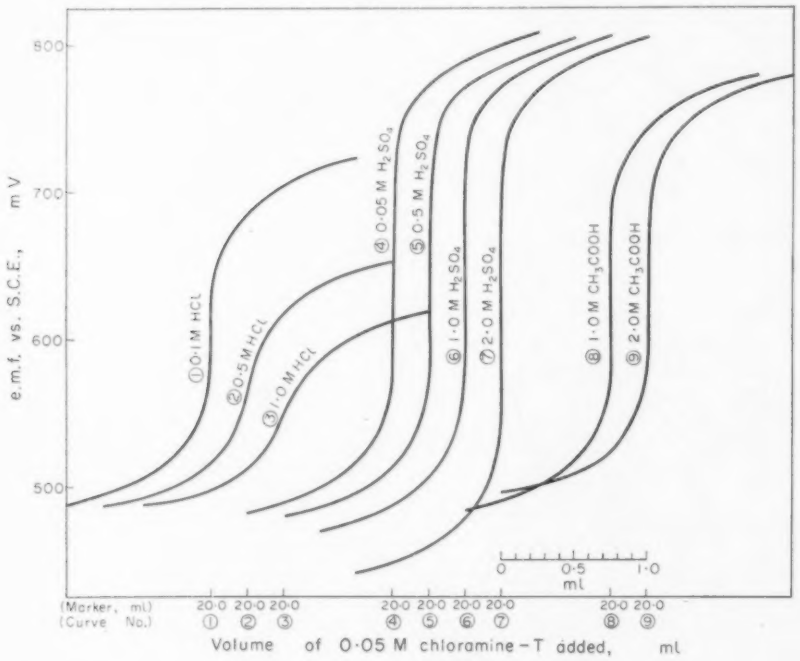

FIG. 1.

In a plain unbuffered aqueous medium, the solution turned yellow after the addition of 1 ml of chloramine-T. Thereafter the colour did not deepen, nor did the potential change by more than a few mV even after the addition of a 15% excess of oxidant. The pH of the solution was then 9·8, which agrees well with previous findings[2] as to the pH at which reaction ceases, and with the amount of hydrogen ion consumed by 1 ml of oxidant. Reaction in this medium is therefore impracticable.

In a phosphate buffer of pH 7·0, iodine was readily liberated, the potentials in the early part of the titration being similar to those recorded in 1·0*M* acetic acid. Over the interval $\pm 5\%$ round the equivalence point, however, there was no potential break, merely a slow drift of 25 mV. The determination of iodide at pH 7 is therefore impracticable even in a buffer medium.

Titrations in the reverse sense were no more successful in either medium. The addition of iodide to an aliquot of chloramine-T produced a yellow colour with the first ml, but this colour practically disappeared within 1 min, and further additions gave no more than the faintest colour. It is possible at the pH of the solution that

iodine either hydrolyses to hypoiodite which then disproportionates, or is oxidised by chloramine-T to iodate, and that the products do not then react with iodide, but the exact explanation is difficult to establish.

This bears additionally on the mechanism of the reaction at pH values up to 10 in the presence of iodide. It has been shown[2] that above pH 6, chloramine-T will oxidise arsenic^{III} only in the presence of iodide. This reaction may be sequential, *i.e.*, chloramine-T first oxidises iodide to iodine, then iodine oxidises arsenic^{III} to arsenic^{V}, in which case the iodine is a reaction intermediate. Alternatively, iodide, or an oxidation product thereof, such as iodine, iodate or an intermediate species, may be a catalyst for the direct reaction between chloramine-T and arsenic^{III}. It is unlikely that the reaction is a heterogeneous chemisorption catalysis since the only solid phase present is represented by the vessel and the electrodes: the concentration of dichloramine is less than micromolar[1] and this species is completely soluble under these conditions. The distinction between a chemical catalyst and a reaction intermediate is purely one of quantity, the former being effective in very small concentration. Where a buffer is available to supply hydrogen ion for reaction, iodine is plentifully liberated, and so may be regarded as a reaction intermediate, but at the upper pH limit of the reaction, or when no buffer is available, only small amounts of iodine are liberated, and the requirement in iodide concentration increases, so iodide could be regarded as a reaction intermediate and iodine as a catalyst. On the whole it appears most satisfactory to regard iodide as a reaction intermediate.

(c) *Direct titration in acid media in the presence of bromide.* Curves 1 to 4 in Fig. 2 illustrate the effect of bromide on the titration. Although the equilibration speed was satisfactory, the addition of bromide is not helpful. The inflections were completely suppressed at a bromide concentration of 0·1*M*, but appeared when the bromide concentration was reduced to 0·01*M*. In hydrochloric acid the flattening is not marked compared with bromide-free media, but the end-point potential change in sulphuric acid is very much decreased, although a sulphuric acid medium yields better curves than a hydrochloric acid medium. Iodide can therefore be determined in the presence of bromide of equal initial concentration, provided this does not exceed 0·01*M*.

(d) *Direct titration in acid media in the presence of arsenic^{III}.* Titration of a mixture of known quantities of arsenic^{III} and iodide solutions in 1·0*M* hydrochloric or sulphuric acids gave curves 5 and 6 in Fig. 2. The end-points were in satisfactory agreement with the theoretical value for the sum of the two reductants. The potentials, surprisingly, accord with the oxidation of iodide as the potential-determining reaction in the end-point region and not, as might have been expected in strong acid media, with the oxidation of arsenic^{III} (*cf.* curves 3 and 6, Fig. 1). The same results were obtained by adding excess chloramine-T to an aliquot of iodide, followed by an aliquot of arsenic^{III} solution (larger than was equivalent to the iodide) and finally titrating with chloramine T. Sulphuric acid again provides much the better medium.

Since arsenic^{III} in bicarbonate buffer in the presence of iodide at a concentration below 0·05*M* can be accurately titrated with chloramine-T either visually[1] or potentiometrically,[2] it is evident that by combining this titration with titration after acidification with, preferably, sulphuric acid, arsenic^{III} and iodide can be successively determined in one solution. Furthermore, the determination of iodide can be accompanied by

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the standardisation of the titrant by the addition of an aliquot of standard arsenic^{III} solution in the same way.

(e) *Reverse titration in acid media.* To test Afanas'ev's claim[6] in respect to the titration of chloramine-T in 0·5*M* sulphuric acid with iodide, aliquots of chloramine-T solution which had been de-oxygenated with nitrogen were added to the required acid solution previously outgassed with carbon dioxide, and titrated with iodide. The titration curves are satisfactory as shown in Fig. 2 at acid concentrations of 0·5*M*

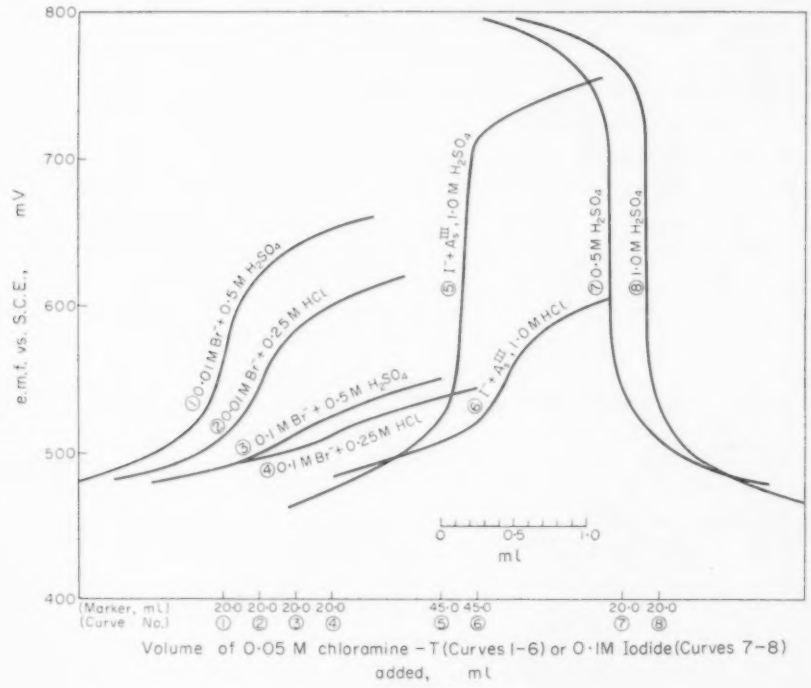
800
700
600
500
400
e.m.f. vs. S.C.E., mV
①0·01 M Br⁻ + 0·5 M H₂SO₄
②0·01 M Br⁻ + 0·25 M HCl
③0·1 M Br⁻ + 0·5 M H₂SO₄
④0·1 M Br⁻ + 0·25 M HCl
⑤ I⁻ + A^{III}, 1·0 M H₂SO₄
⑥ I⁻ + A^{III}, 1·0 M HCl
⑦0·5 M H₂SO₄
⑧1·0 M H₂SO₄
0
0·5
1·0
ml
(Marker, ml.) 20·0 20·0 20·0 20·0 45·0 45·0 20·0 20·0
(Curve No.) ① ② ③ ④ ⑤ ⑥ ⑦ ⑧
Volume of 0·05 M chloramine-T (Curves 1–6) or 0·1M Iodide (Curves 7–8) added, ml

FIG. 2.

and 1·0*M*, but at an acid concentration of 0·05*M* the reaction was too slow to be followed. Dichloramine-T was precipitated on the addition of chloramine-T to the acid medium, and slowly dissolved as the reaction proceeded. Through the interval of 1·0 ml before the equivalence point, the potential after each increment of iodide fell swiftly and recovered slowly. Though the curves are satisfactory, the end-points are about 0·4% early, the error being independent of time and acid concentration and not therefore caused by loss of oxidant. Nor is the error caused by induced oxidation of iodide because it would then be positive. This sense of titration cannot therefore be regarded as satisfactory.

2. *Oxidation to monopositive iodine*

In Andrews-type reactions, *i.e.*, those in which monopositive iodine is formed by oxidation and stabilised by combination with chloride ion as iodine monochloride, it is convenient to provide the stabilisation by means of hydrochloric acid. A lower limit to the required hydrochloric acid concentration is set by dissociation of the iodine monochloride in falling chloride concentration and hydrolysis of the I^+ ions

so formed in falling hydrogen ion concentration. The two are interrelated and it is possible to conduct such titrations at low hydrogen ion concentrations in the presence of high chloride ion concentrations (or cyanide or bromide) and *vice versa*. An upper limit to the hydrochloric acid concentration may be set by the effect of hydrogen ion on the potential of the reductant system, combined with the katagenic effect of chloride ion on the monopositive iodine potential. The present examination was restricted to hydrochloric acid media, and the concentrations varied over a wide range. In the fully oxidised solution, the iodine colour is replaced by the pale yellow of iodine monochloride and it becomes possible to use visual indicators as well as potentiometric methods to locate the end-point.

(a) *Potentiometric titrations.* Curves for potentiometric titrations in 1·0*M* to 5·0*M* hydrochloric acid are shown in Fig. 3, and the results are given in Table I.

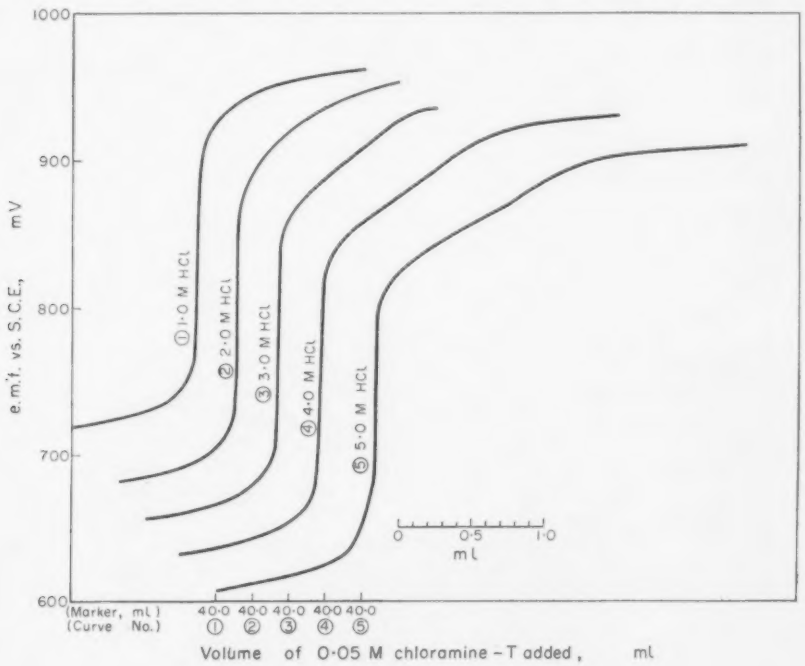

FIG. 3.

Although the potentials reached equilibrium quickly and the end-points are sharp, the curves are a little ragged. The results are good in the range 3–4*M* acid, but the end-points are premature in more dilute acid and late in more concentrated acid. In fact the consumption of oxidant increases progressively with increasing acid concentration, and it is correct over only a narrow range. This steady increase is not caused by an impurity in the hydrochloric acid, as will be shown later: there is a trace of titratable substance in this reagent, but its nature is such that the inflection lies at very much higher potentials than those here recorded.

(b) *Titration with carbon tetrachloride as visual indicator.* Carbon tetrachloride is not the most convenient indicator; chloroform, with a lower partition coefficient permits faster reaction at the end-point; but with due allowance in longer time of

shaking carbon tetrachloride gives rather more accurate results in Andrews titrations, and was used in this work. The end-points in 1·0*M* to 5·0*M* hydrochloric acid were all quite sharp and satisfactory, as the results show. Once again there is an increase in consumption of oxidant with increasing acid concentration, though only 0·1% compared with 0·5% by the potentiometric method. It is difficult to account for this discrepancy. For the best results, the concentration of hydrochloric acid should be 3·0*M* to 4·0*M*, and the end-point detection with carbon tetrachloride is preferred.

These determinations correspond to a quantity of 20 ml of 0·1*M* iodine monochloride, and although the errors sharply restrict the hydrochloric acid concentration range in the determination of iodide, these errors are greatly reduced when much smaller quantities of iodine monochloride are used as a reaction intermediate in other determinations, and should fall within the experimental error over the range 2·0*M* to 4·0*M* hydrochloric acid for 2 to 5 ml of 0·1*M* iodine monochloride.

Zusammenfassung—Die Oxydation von Jodid zu Jod und monopositivem Jodion mit Chloramin-T wurde über einen breiten Bereich wechselnder Bedingungen studiert. Zur Oxydation zu freiem Jod wird Schwefelsäure und Essigsäure in einer Konzentration von 1,0 m als bestes Medium empfohlen. Salzsäure ist viel weniger gut geeignet. Die umgekehrte Titration (d.h. Zugabe von Jodid zur angesäuerten Chloramin-T-Lösung) gibt negative Fehler und ist nicht geeignet. Titration in neutralem Medium (gepuffert oder ungepuffert) ist abzuraten. Bromid bis zu einer maximalen Konzentration von 0,01 m verursacht in schwefelsäurem Medium keine Störung. Arsen(III) und Jodid können in einer Mischung nacheinander titriert werden.

Oxydation zu Jodmonochlorid verläuft nur in 3·0–4·0 m Salzsäure quantitativ. Die Titration wird besser mit Kohlenstoff-tetrachlorid unter visueller Extraktionsindication vollzogen als potentiometrisch.

Resumé—Les auteurs ont étudié l'oxydation par la chloramine-T de l'iodure en iode libre et en ion positif monovalant dans de nombreuses conditions. Pour l'oxydation en iode libre, les milieux acide sulfurique ou acétique conviennent, une concentration 1,0 M est recommandée. L'acide chlorhydrique convient beaucoup moins bien. Le titrage inverse (addition d'iodure à la chloramine-T acidifiée) est sujet à des erreurs par défaut considérables et n'est pas recommandé. Le titrage en solution neutre, temponnée ou non, est irréalisable. Du bromure de concentration maximale 0,01 M peut être présent, en particulier en milieu acide sulfurique, sans causer d'erreur. De l'arsenic (III) et de l'iodure mélangés peuvent être dosés successivement.

L'oxydation en monochlorure d'iode est quantitative seulement dans le domaine de concentration d'acide chlorhydrique 3–4 M; elle est mieux réalisée avec le tétrachlorure de carbone comme indicateur visuel que par la méthode potentiométrique.

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UNTERSUCHUNG DER KATIONENSORPTION AUS KOMPLEXANMEDIUM—II*

CHROMATOGRAPHISCHE TRENNUNG DES CALCIUMS UND STRONTIUMS

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Zusammenfassung—Es wurde die Trennung des Calciums von Strontium auf chromatographischem Wege ausgearbeitet. Die vorstehenden zunächst an Kationenaustauscher adsorbierten Kationen lassen sich mittels einer 0,02–0,05 m Lösung von 1·2-Diaminocyclohexan-N.N.N′.N′-tetraessigsäure (DCyTE) in 0,4 m Ammoniumacetat (pH 5,1) stufenweise nacheinander auswaschen. Unter diesen Bedingungen wird zunächst Calcium und erst nach dem Durchgang von etwa 400 ml der 0,05 m Waschlösung auch Strontium ausgewaschen. Mit Hilfe dieser Methode wurden Calcium und Strontium in den verschiedensten Konzentrationverhältnissen voneinander getrennt; so wurden z.B. 1000 μg Strontium von 200 mg Calcium (d.h. im Verhältnis von 1:200) mit einem Fehler von $\pm 1\%$ getrennt.

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DIE schwierige Trennung der Erdalkalien mittels klassischer analytischer Methoden wurde bisher nicht zufriedenstellend gelöst. Die genaue und verlässliche Bestimmung von Strontium in überschüssigem Calcium stellt ein wichtiges Hilfsmittel der Bestimmung des absoluten Alters von Gesteinen und der genauen Klassifizierung einiger Mineralarten. Hand in Hand mit der Entwicklung der Kerntechnik hat auch die analytische Chemie des Strontiums und Bariums gewaltig an Bedeutung zugenommen. Zur erfolgreichen Lösung aller diesen Fragen wurden vor allem schnelle und verlässliche Trennmethoden für die einzelnen Glieder der Erdalkalireihe gesucht. Als besonders vorteilhaft erwies sich die Ionenaustausch-Technik und zwar die chromatographische Trennung von an Kationenaustauschern adsorbierten Metallionen mit verschiedenen Auswaschmitteln. Zur Trennung von Erdalkalien wurden ausser Mineralsäuren hauptsächlich einige organische Oxysäuren wie Wein-, Citronen-, Milch-, α-Hydroxyisobuttersäure u. ä. vorgeschlagen. Ein sehr wirksammes Trennmittel für solche Chromatographie stellt auch die Äthylendiamintetraessigsäure—ÄDTE—dar. Die letztere wird entweder als Auswaschmittel verwendet oder werden die Erdalkalien aus ÄDTE-Medium bei verschiedenem pH ausgewaschen.

Die grundlegende Arbeit über die Trennung des Strontiums und Bariums stellt die Untersuchung von Bovy und Duyckaerts[1] dar, in der die Beziehung zwischen dem Verteilungskoeffizient und den Komplexbildungskonstanten der entsprechenden Chelate abgeleitet wird. Mit Hilfe ähnlicher Chromatographie gelang es auch Fouarge und Fuger,[2] Calcium, Strontium, Barium und Radium voneinander abzutrennen. Die Sorbierbarkeit der Erdalkalien aus ÄDTE-Medium in Abhängigkeit vom pH-Wert untersuchten auch Taketatsu[3] bzw. Nikolskij und Trofimov.[4]

* Part I—see ref. 16.

Mit der chromatographischen Trennung des Calciums und Strontiums mit ÄDTE-Lösung befasste sich Myers[5]; die gleichzeitige Trennung von Calcium, Strontium, Barium und Radium mit Hilfe der gleichen Technik wurde von Duyckaerts und Lejeune[6] beschrieben. Zur chromatographischen Trennung einiger Metalle bei der Analyse des ausgebrannten Kernmaterials wurde ÄDTE bei verschiedenen pH-Werten von Honda[7] verwendet. Einen oft untersuchten Gegenstand stellen auch die Arbeiten über die selektive Sorption von Metallen aus ÄDTE-Medium, wie z.B. die Trennung des Strontiums von überschüssigem Calcium[8,9] oder die Trennung des Radiums von überschüssigem Barium[10]. Die gleiche Technik wurde auch zur Bestimmung von Strontium, evtl. Barium und Radium in Boden[11], Trinkwasser[12] oder biologischem Material[13] herangezogen.

Zur Trennung der Erdalkalien erwiesen sich auch Anionenaustauscher im ÄDTE-Cyclus brauchbar.[14] In dieser Weise wurden durch Auswaschen mit gepufferten ÄDTE-Lösungen Calcium und Strontium voneinander getrannt.[15] In der vorangehenden Arbeit[16] zeigten wir, dass ein besseres Auswaschmittel als ÄDTE die 1.2-Diaminocyclohexan-N.N.N′.N′-tetraessigsäure, DCyTE, die bisher nur zur selektiven Trennung des Mangans[17] von den Erdalkalien verwendet wurde, darstellt. Die Sorptionskurven der Erdalkalien aus DCyTE-Medium weisen in der pH-Abhängigkeit grössere Unterschiede als die Sorptionskurven der entsprechenden ÄDTE-Komplexe auf. Dadurch ist die Voraussetzung einer besseren Trennung der Erdalkalien, insbesondere des Calciums und Strontiums und zwar auch in extremen Konzentrationsverhältnissen, gegeben.

VERSUCHSTEIL

Verwendete Apparate und Reagenzien

Die Bestimmung von Strontium und Calcium erfolgte durch Aufnahme des Molekularbandspektrums mit Hilfe des Flammenphotometers Zeiss III unter Anwendung des Li-Filters mit maximaler Durchlässigkeit von 665–687 mμ im Falle des Strontiums und eines Filters mit maximaler Durchlässigkeit von 620–630 mμ im Falle des Calciums. Die Lösung wurde in Luft-Acetylen-Flamme bei 0,4 at und 40 mm Wassersäule angeregt.

Sämtliche pH-Messungen wurden mit Hilfe des Titrimeters TTT-1 der Firma Radiometr, Kopenhagen, Dänemark, durchgeführt. Um dem Auslaugen von Kationen aus Glas vorzubeugen, wurde das Abdampfen und die Oxydation von Komplexanen in Quarzgefässen durchgeführt. Die 1m Lösung von Ammoniumacetat wurde durch Neutralisieren von 60 g Eisessig in 500 ml destilliertem Wasser mit verdünntem Ammoniak (1:1) bis zum pH 5,1 und durch anschliessendes Auffüllen zu 1 Liter hergestellt.

Die Komplexbildner—die Äthylendiamintetraessigsäure und die 1.2-Diaminocyclohexan-N.N.N′.N′-tetraessigsäure wurden durch mehrmaliges Umfällen aus 10%iger Salzsäure, Auswaschen mit Wasser und Trocknen bei 50°C gereinigt. Ihre 0,02m bzw 0,05m Lösungen wurden durch Neutralisieren der wässrigen Suspension mit verdünntem Ammoniak (1:1) bereitet.

Die Standartlösungen der Erdalkalien wurden aus spektral reinen Ca- bzw. Sr-Präparaten hergestellt. Die letzteren wurden durch Reinigung[18] der handelsüblichen pro Analysi Präparate gewonnen. Ammoniumhydroxyd wurde durch Sättigen von deionisiertem Wasser mit Ammoniakgas bereitet.

Es wurde an einem stark sauren Kationenaustauscher, Amberlit IR-120, im Ammoniakcyclus gearbeitet. Die Korngrösse des Ionenaustauschers bzw. die Grösse der Kolonne siehe[16]. Zum Studium der Sorption aus Komplexanmedium wurden Füllungen von 25 ml verwendet.

ERGEBNISSE

Wir untersuchten zunächst gesondert das Verhalten von Calcium und Strontium bei dem Auswaschen mit DCyTE bei verschiedenen pH-Werten. Die Auswaschlösungen wurden so hergestellt, dass sie 0,02 bzw. 0,05 m an DCyTE und 0,4 m an

Ammoniumacetat waren; der gewünschte pH-Wert wurde mit Essigsäure bzw. mit Ammoniak unter potentiometrischer Kontrolle eingestellt.

Die Calcium- bzw. Strontiumstandartlösungen wurden aus einem kleinen Volumen am Ionenaustauscher adsorbiert und die Kolonne wurde jeweils mit 50 ml Wasser ausgewaschen. Hierauf wurde mit dem Auswaschen begonnen; bei einer Geschwindigkeit der Auswaschlösung von 1–1,5 ml. min^{-1}. cm^{-2} wurden Fraktionen von 25 ml aufgefangen. Diese Fraktionen wurden durch Abdampfen zur Trockne mit 20 ml konz. Salpetersäure mineralisiert, in 3 ml konz. Salzsäure aufgenommen, im 25 ml Messkolben aufgefüllt und ihr Gehalt an Strontium bzw. Calcium flammenphotometrisch ermittelt. Die Ergebnisse dieser Bestimmungen sind in Abbildung 1 wiedergegeben. Das Auswaschen des Strontiums wurde bei pH 5,1 bis zur 20. Fraktion verfolgt. Spuren von Strontium erscheinen erst in der 16. Fraktion. Das Auswaschen von Strontium bei diesem pH-Wert ist sehr langsam. Wenn alles Strontium ausgewaschen werden soll, ist es nötig, mit 0,02 m DCyTE bzw. 0.02 m ÄDTE oberhalb pH 6,6 auszuwaschen.

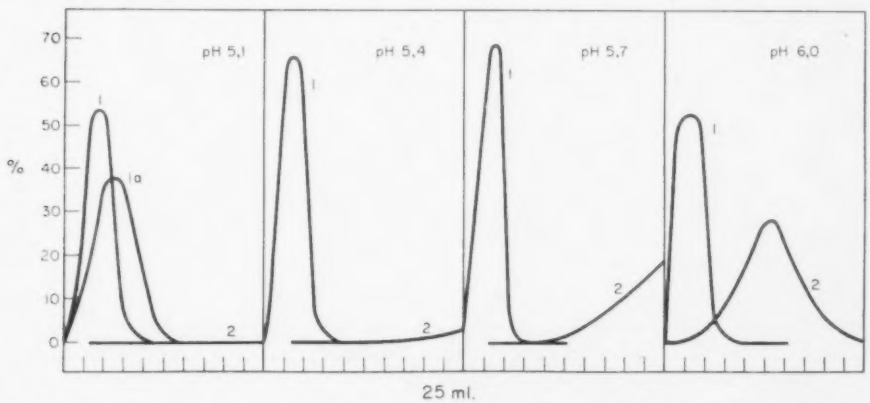

Abb. 1. Auswaschen von Calcium (Kurven 1, 1a) und Strontium (Kurven 2) mit 0,02 m DCyTE Lösung in Abhängigkeit vom pH-Wert.
Amberlite IR-120, NH_4, 0,15–0,30 mm, 1 $cm^2 \times 25$ ml. Auswaschgeschwindigkeit 1,5 ml. min^{-1} cm^{-2}. Analysiert wurden Fraktionen zu 25 ml. Ordinate: ausgewaschene Prozente des Metallions. Ca — 20 mg (1a–40 mg) Sr — 22 mg.

Aus Abbildung 1 ist ersichtlich, dass der pH-Wert von 5,1 eine Grenze darstellt, bei der sich Calcium von Strontium und wie im weiteren festgestellt wurde auch von Barium verlässlich trennen lässt. Die Bildung der Calcium-DCyTE-Komplexe verläuft verhältnismässig schnell, so dass sich z.B. 100 mg Calcium mit 125 ml 0,05 m DCyTE quantitattiv auswaschen lassen. Das Strontium erscheint bei diesem pH-Wert erst in der 16. Fraktion, d.h. nach dem Durchlaufen von 375 ml Waschlösung. Zwischen den Grenzen der beiden Banden liegt also ein Volumen von wenigstens 175–200 ml Waschlösung, was zur scharfen Abtrennung vollkommen ausreicht. Eine noch schärfere Trennung erreicht man durch Anwendung von feiner gekörntem Ionenaustauscher. Dies hat jedoch auf der anderen Seite eine Abnahme der Durchlaufgeschwindigkeit zur Folge. Da bei der Komplexbildung beträchtliche Mengen Wasserstoffionen frei werden, muss zur Einhaltung des pH-Wertes der Puffer in 0,4 molaren Konzentration verwendet werden.

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Auf Grund der obigen Erfahrungen wurde die Trennung von Calcium und Strontium in synthetischen Proben durchgeführt. Nach der Sorption am Ionenaustauscher wurde die Kolonne mit 50 ml Wasser ausgewaschen und hierauf Calcium mit 100 ml 0,02 m DCyTE-Lösung von pH 5,1 und anschliessend Strontium mit der gleichen Lösung von pH 7,2 bei konstanter Geschwindigkeit von 1,5 ml. min^{-1}. cm^{-2} eluiert. Die erhaltenen Fraktionen wurden mit Salpetersäure mineralisiert und ihr Gehalt flammenphotometrisch ermittelt. Die Messergebnisse (Tabelle 1) wurden

TAB. I. CHROMATOGRAPHISCHE TRENNUNG VON CALCIUM UND STRONTIUM MIT 0,02 m DCyTE BEI pH 5,1 Sr = 3,94 mg

Probe	Ca, *mg*		Δ%	Ca:Sr
	gegeben	gefunden		
1	0,39	0,39	—	1:10
2	0,98	0,98	—	1:4
3	1,97	1,90	−3,5	1:2
4	2,95	3,10	5,1	1:1,3
5	3,93	3,93	—	1:1
6	5,11	5,20	1,7	1,3:1
7	6,29	6,20	−1,4	1,6:1
8	7,47	7,38	−1,2	1,9:1
1–8	3,94	3,94 ± 0,05	±1,3	Sr-Bestimmung

mit Werten der unter den gleichen Bedingungen gemessenen Standartlösungen verglichen. Die Bestimmungsfehler, im Durchschnitt von ±3% rel. sind eher auf Fehler der flammenphotometrischen Bestimmung als auf Fehler der Trennug zurückzuführen.

DIE BESTIMMUNG VON STRONTIUM IN ÜBERSCHÜSSIGEM CALCIUM

Die verhältnismässig grossen Unterschiede der Calcium-bzw. Strontium-DCyTE-Komplexe bei pH 5,1 wurden auch zur Trennung von einem grossen Überschuss des Calciums von wenig Strontium ausgenutzt. Die Metalle wurden aus 80–100 ml Lösung, die neben 200 mg Calcium noch verschieden grosse Mengen Strontium enthielt, am Ionenaustauscher adsorbiert. Nach dem Auswaschen der Säule mit 50 ml Wasser und 20 ml 0,4 m Ammoniumacetat (pH 5,1) wurde Calcium mit 200 ml 0,05 m DCyTE im gleichen Puffer ausgewaschen. Der Ionenaustauscher wurde mit 30–50 ml destilliertem Wasser ausgewaschen und das Strontium wurde dann mit 10 ml 0,05 m ÄDTE und 20 ml Schwarzenbachschem Puffer[16] eluiert. Die Säule wurde mit Wasser in Quarzgefässe so ausgewaschen, dass das Volumen des Eluiermittels und der Waschflüssigkeit kleiner als 100 ml war. Nach dem Einengen auf etwa 30 ml wurde die Mineralisierung mit 20 ml destillierter konzentrierter Salpetersäure durchgeführt. Die unter stürmischer Gasentwicklung verlaufende Oxydation wurde durch Zusatz von weiteren 20 ml konzentrierter Säure beendet. Hierauf wurde die Lösung zur Trockne abgedampft, mit 1 ml konzentrierter Salzsäure zweimal befeuchtet und erneut zur Trockne abgedampft. Der Abdampfrückstand wurde mit 2–4 ml konzentrierter Salzsäure versetzt, die ausgeschiedenen Salze wurden in destilliertem Wasser gelöst und die entstandene Lösung wurde dann in einen 25–50 ml fassenden Messkolben übergeführt. Der Strontiumgehalt wurde flammenphotometrisch ermittelt. Die Standartlösungen wurden in analoger Weise, d.h. durch Oxydation mit Salpetersäure bei Gegenwart von ÄDTE und Schwarzenbachschem Puffer bereitet.

Aus den in Tabelle 2 angeführten Ergebnissen geht hervor, dass eine verlässliche Trennung von Strontium bis zum Verhältnis von Calcium zu Strontium 2,000: 1 bei

absolutem Gehalt an Strontium von 100 μg möglich ist. Die Hauptfehlerquelle bilden Verunreinigungen aus Salpetersäure, die zur Mineralisierung verwender wird, und daher vor der Verwendung umdestilliert werden muss. Bei sorgfältiger Arbeit ist die Calciummenge in der Strontiumfraktion kleiner als 0,1 mg, d.h. weniger als 0,05% Ca von den ursprünglichen 200 mg.

TAB. II. BESTIMMUNG KLEINER MENGEN STRONTIUM IN ÜBERSCHÜSSIGEM CALCIUM
Ca = 200 mg

Sr, *mg*		Differenz %
gegeben	gefunden	
5,00	4,93	−1,4
5,00	5,05	1,0
4,00	4,02	0,5
3,00	3,02	0,7
2,00	1,98	−1,0
1,00	1,01	1,0
0,75	0,75	0,0
0,50	$0{,}50_8$	1,6
0,20	$0{,}20_8$	4,0
0,10	0,11	10,0

Gleichzeitig mit Calcium wird auch Magnesium ausgewaschen. Mit DCyTE in 0,4 m Acetatpuffer (pH 5,1) wird Magnesium viel besser als mit ÄDTE ausgewaschen.[16] Die gleichzeitige Anwesenheit weiterer Metallionen wie z.B. von Eisen, Mangan, Aluminium, Titan, Blei, Zink, Kupfer, Uran, Nickel, Kobalt und von vielen anderen stört die Trennung nicht, da die genannten Metallionen mit DCyTE bei pH 5,1 sehr feste Anionenkomplexe liefern, die gleichzeitig aus der Säule mit Calcium ausgewaschen werden.

Die vorgeschlagene Trennung des Calciums von Strontium wurde bei der Bestimmung dieser Elemente in natürlichem Material und in Mineralwasser verwendet.[18] Die gleiche Methodik ist auch zur Isolierung von Strontium 90 aus verschiedenem Material anwendbar.

Summary—The separation of calcium from strontium has been carried out chromatographically. The cations after sorption on a cation-exchanger, are eluted stepwise by means of a 0·02–0·05*M* solution of 1,2-diaminocyclohexane-N,N,N′,N′-tetra-acetic acid (DCyTE) in 0·4*M* ammonium acetate at pH 5·1. Under these conditions calcium is first eluted, and after about 400 ml, strontium. By means of this method 1 mg of strontium can be separated from 200 mg of calcium (*i.e.*, a ratio of 1:200) with an error of 1%.

Résumé—La séparation du calcium et du strontium a été réalisée par chromatographie. Les cations après fixation sur un échangeur de cations, sont élués graduellement au moyen d'une solution 0,02–0,05 M d'acide 1,2-diamine-cyclohexane N N N′ N′ tétracétique (D Cy T E) dans l'acétate d'ammonium 0,4 M à pH 5,1. Dans ces conditions, le calcium est élué en premier, et ensuite le strontium après passage d'environ 400 ml de solution. Par cette méthode on peut séparer 1 mg de strontium de 200 mg de calcium (c'est-à-dire un rapport de 1/200) avec une erreur de 1%.

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THE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF SILVER

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Summary—Pyrogallol red may be used as a reagent for the spectrophotometric determination of silver ions in dilute solution. The reagent forms a yellow complex, $[Ag_2(C_{19}H_8O_8S)]^{2-}$, the colour of which is stable for at least 24 hr. Optical density measurements at 390 mμ show that at pH 7–7·5 Beer's law is obeyed over the range up to 85 μg of Ag^+. The colour system is unaffected by normal laboratory variations in temperature or lighting conditions and no special purification of reagents is necessary. None of the common anions interferes except the halides. Most cations interfere, but this is readily prevented by the addition of an amount of EDTA equivalent to the total molar concentration of the other metal ions. This total can readily be determined by a simple titration process on a separate aliquot of solution without separating the silver ions. The method appears to be more reproducible than the standard dithizone method.

Bromopyrogallol red may be used similarly with measurements made at *ca.* 440 mμ.

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THERE is a dearth of satisfactory spectrophotometric methods for the determination of silver ions in very dilute (*ca.* $10^{-6}M$) solutions. The most commonly used reagents are *p*-dimethylaminobenzalrhodanine and dithizone.[1] The former is fairly selective in its action, but is troublesome in many respects. It reacts with silver in acidic media to give a coloured complex or a precipitate which is usually measured spectrophotometrically at *ca.* 470 mμ. Different authors recommend a variety of different conditions resulting in the formation either of a precipitate with considerable colour or alternatively of little precipitate and little colour. The colour system is very susceptible to changes in acidity and it is our experience that unaccountable results are not infrequent.

Silver dithizonate is normally extracted into carbon tetrachloride from acid solution and its absorption in the extract is measured at 460 mμ. For trace amounts of silver, however, the undue susceptibility of the reagent solution to photodecomposition, oxidation to diphenylthiocarbadiazone and the influence of changes in temperature combine to cause non–reproducibility from day to day.

Catalytic methods offer high sensitivity, but demand rigid control of experimental conditions, and are generally very susceptible to interference from other ions.

Bearing these limitations in mind and as a result of it being necessary for us to find a more reliable method for following the behaviour of traces of silver ions in extraction experiments, we have undertaken an examination of the colour systems formed by silver ions with eighteen metallochromic reagents including Solochrome Black T, *o*-Cresolphthalein complexan, P.A.N., P.A.R., Catechol violet, Glycine thymol blue, Pyrogallol red, Bromopyrogallol red, *etc.* As a result of this examination, it was concluded that the two last mentioned dyestuffs were alone worthy of detailed examination. This paper describes the application of both reagents to the determination of silver in aqueous solution. A later paper will discuss the application of one of them to the direct colorimetry in organic media of silver extracted by a selective new extraction system.[2]

The preparation of Pyrogallol red, (*cf.* Fig. I) was first reported in 1898 by Sohon,[3]

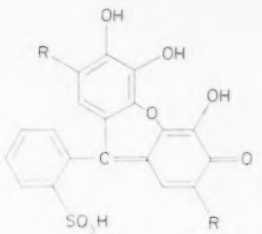

FIG. 1.—Pyrogallol red, R = H.
Bromopyrogallol red, R = Br.

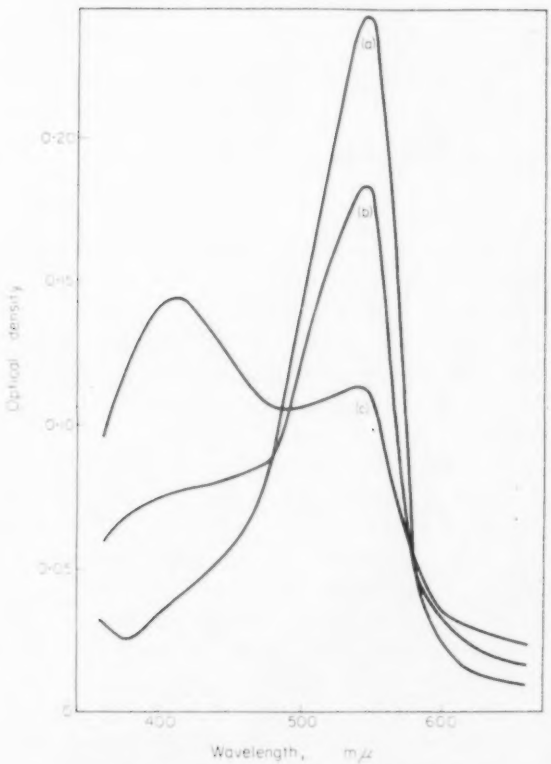

FIG. 2.—Silver-Pyrogallol red colour system
(*a*) 10 ml of $10^{-4}M$ Pyrogallol red buffered at pH 7 and diluted to 100 ml.
(*b*) As (*a*), but plus 10 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.
(*c*) As (*a*), but plus 20 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.

who obtained it by condensation of *o*-sulphobenzoic anhydride with pyrogallol. The dye and its dibromo-derivative, are now available commercially as a result of their use by Suk, Malat and Jenickova[4] as complexometric indicators for the ethylenediamine-tetra-acetate titration of several metal ions, including Bi, Ni, Co, Pb, Cd, Mg, Mn^{II}, Ce^{III} and the rare earths under a variety of pH conditions. Several other ions form coloured products, *e.g.*, Cu^{II} and Ag, though these cannot be utilised for indicator purposes. Both reagents have been advocated by Vodák and Leminger[5] as spot-test reagents for the detection of silver ions, but the test is subject to interference from

practically all cations except those of the alkali metals. Both dyes are slightly soluble in ethanol, but insoluble in other organic solvents. In dilute aqueous solution they exhibit an orange-yellow colour in mineral acid solution, claret-red in near-neutral solution and violet in alkaline media. Pyrogallol red unlike its dibrominated derivative is markedly unstable in solutions of high pH, though otherwise quite stable.

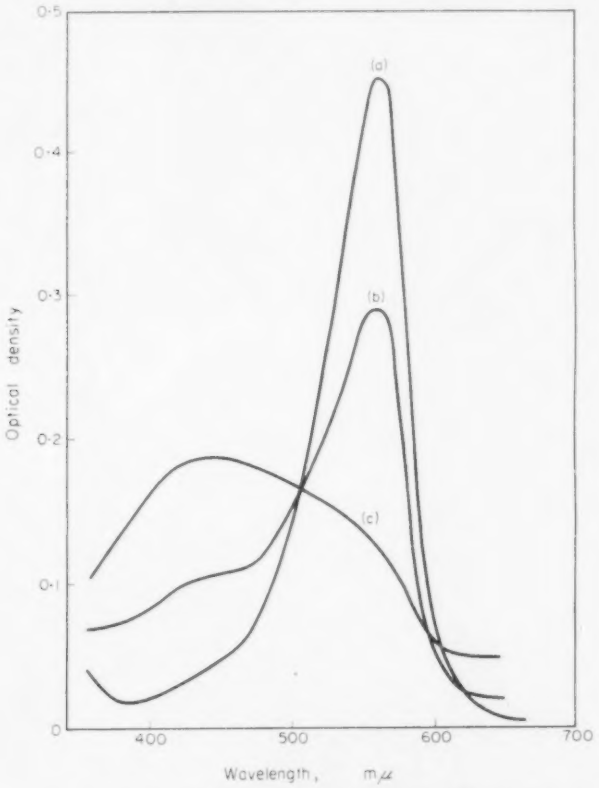

FIG. 3.—Silver-Bromopyrogallol colour red system
(*a*) 10 ml of $10^{-4}M$ Bromopyrogallol red at pH 7 diluted to 100 ml.
(*b*) As (*a*) but plus 10 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.
(*c*) As (*a*) but plus 20 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.

It was found in preliminary experiments that both reagents reacted best with silver around pH 7, when the claret-red colour of the reagent underwent a change to a less intensely absorbing greenish-yellow coloured solution together with a slight colloidal suspension (especially apparent at high concentrations of silver). Figs. 2 and 3 were obtained with a Unicam SP 600 spectrophotometer (10-mm path) using (*a*) 10 ml of the appropriate reagent in 10^{-4} *M* solution in 50% v/v aqueous ethanol; (*b*) with the addition of an equimolar amount of silver ion; and (*c*) a two-molar ratio of silver ion. In each case the solution was buffered with 20% sodium acetate to pH $\approx$ 7 and diluted to 100 ml. In each case, it will be observed that the addition of silver decreases and practically eliminates the band absorption *ca.* 550 mμ and builds up another band absorbing *ca.* 410–420 mμ. The results represented by Figs. 2 and 3 were obtained after a reaction time of 30 min. Subsequently it was found

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that longer standing caused increased optical densities at the silver peaks *ca.* 410 mμ and decreased absorption at the reagent peaks *ca.* 550 mμ. Further experiments established that the optimum conditions were obtained after 1·5 hr standing time and that for maximum colour formation it was desirable not to dilute the solutions to 100 ml till this time had elapsed. The "blank" solutions were quite stable, and it was

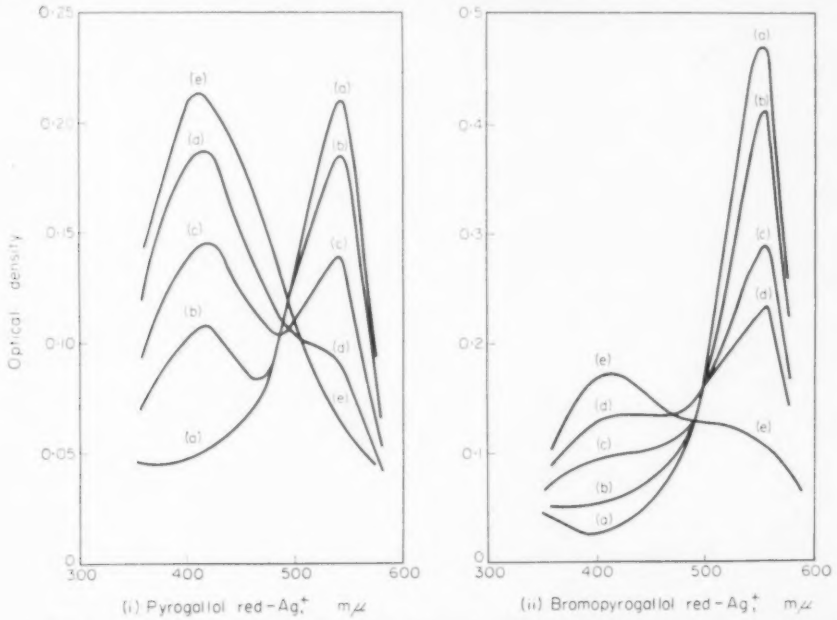

FIG. 4.—Comparison of Pyrogallol red and Bromopyrogallol red under optimum conditions
Standard time of development 90 min *before* dilution.
(*a*) 10 ml of reagent.
(*b*) 10 ml of reagent +5 ml of $10^{-4}M$ $AgNO_3$.
(*c*) 10 ml of reagent +10 ml of $10^{-4}M$ $AgNO_3$.
(*d*) 10 ml of reagent +15 ml of $10^{-4}M$ $AgNO_3$.
(*e*) 10 ml of reagent +20 ml of $10^{-4}M$ $AgNO_3$.

found that the absorption at the silver peaks exhibited maximum stability; the absorption *ca.* 400 mμ remained unchanged for several days.

An attempt was now made to establish which reagent was to be preferred for the determination of silver and to ascertain whether it was best to measure the decrease in absorption of the reagent bands *ca.* 550 mμ or the silver bands *ca.* 400 mμ. The best pH range for Pyrogallol red was found to be 7–7·5 and for Bromopyrogallol red the best value was 7·5. Using these optimum conditions, varying amounts of $10^{-4}M$ silver nitrate were added to constant amounts of the two reagents and the results obtained (*cf.* Fig. 4) show that at the most stable peak, *ca.* 400 mμ, the Pyrogallol red reagent is the more sensitive. In addition, a 2:1 complex [$(Ag)_2$ Pyrogallol red] or [$(Ag)_2$ Bromopyrogallol red] is suggested by the observation that ratios of silver to reagent greater than two cause no further increase in the optical density of the solution.

A continuous variations plot with 10^{-4} *M* Pyrogallol red and silver nitrate solutions at 390 mμ* (*cf.* Fig. 5) shows a clear indication of a 2:1 silver-reagent complex.

* 390 mμ represents the wavelength of maximum separation between the absorption curves for the reagent and its silver complex.

Similar results were obtained with Bromopyrogallol red when measurements were made at 440 mμ.

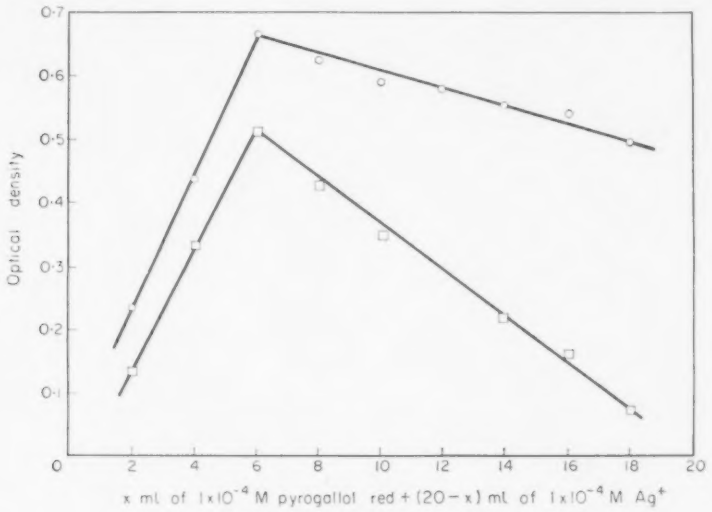

FIG. 5.—Job Plot of Silver—Pyrogallol red system (390 mμ)
(*a*) Experimentally obtained curve.
(*b*) Curve corrected for reagent background.
Point of maximum absorbance, Ag/reagent = 2·2/1

A calibration curve was next obtained by the procedure recommended under *Experimental*. It is represented by a straight line passing through the origin. Beer's law is obeyed up to 85 μg of silver. The interference of a selected range of cations *viz.*, Hg^{II}, Cu^{II}, Al, Zn, Pb, Mg, Ca, Ba, was examined, and not unexpectedly, all were found to interfere by reacting with the reagent. All these complexes are broken down by EDTA, but though silver only forms a weak complex (Log $K \approx 10^{-7}$) with the complexan it is also partially attacked; masking by the addition of excess of EDTA is therefore not possible. Similar attempts to utilise weak complexans such as iminodiacetic acid and anthranilic acid diacetic acid also failed, though they caused much less interference with the silver-Pyrogallol red colour system. The most successful method of overcoming the interferences was to add an amount of EDTA equivalent to the molar concentration of these foreign cations. This amount can readily be established in most instances by a process of pretitration on an aliquot sample of the solution. Silver does not interfere with EDTA titrations at pH < 7 and in the titration of calcium and magnesium it can readily be masked by cyanide ion. Only with aluminium was difficulty experienced, because of the lack of an indicator sufficiently reliable at low dilutions. The use of a suitable indicator or other means of detecting the end-point would probably eliminate its interference in the same way. The interference of copper cannot be overcome in this manner because of the colour of the Cu^{II}-EDTA complex and the stability of the Cu-Pyrogallol red compound. Table I shows the interference of ten-fold molar ratios of these cations and the removal of such interference by the addition of the requisite amount of EDTA, this latter value having been obtained by direct complexometric titration of the foreign ion in the presence of the silver without separation. It will be seen that in most of these

TABLE I. MASKING OF INTERFERING IONS*

Cation nitrate, *ca.* $10^{-3}M$.	Titration system		Colour change	Amount of $10^{-3}M$ EDTA, *ml*	Solutions	Optical density, 4-cm cuvettes, 390 mμ
	Indicator	Buffer				
Hg[11]	Xylenol Orange[6]	Pyridine, pH 6	Claret → yellow (good)	0·94	(a) Ag only (b) Ag + ion (c) EDTA added	0·111 0·172 0·111
Pb	Xylenol Orange[6]	Acetate, pH 5	Claret → yellow (good)	0·95	(a) (b) As above (c)	0·132 0·046 0·133
Zn	Xylenol Orange[6]	Acetate, pH 5	Purple → yellow (fair)	1·06	(a) (b) As above (c)	0·118 0·148 0·118
Ca	Acid Alizarin Black SN[7]	NaOH, pH 12 + 5% KCN	Claret → blue (good)	0·93	(a) (b) As above (c)	0·126 0·133 0·129
Cu[11]	*o*-Dianisidine-tetra-acetic acid[8]	Acetate, pH 6	Fluorescent (fair)	1·06	(a) (b) As above (c)	0·135 0·025 0·109
Al	Chrome Azurol S[9]	Acetate, pH 4 80°	Violet → orange-red (poor)	0·82	(a) (b) As above (c)	0·126 0·008 0·073
Mg	Solochrome Black 6B[10]	Ammonia, pH 10 + 5% KCN	Claret → blue (fair)	1·08	(a) (b) As above (c)	0·126 0·130 0·128

* The amount of silver taken in these experiments was *ca.* 30–40 μg. In each case a ten-fold molar ratio of the interfering cation was added.

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experiments the interference has been completely eliminated. The interference of other cations, most of which could also be complexed preferentially with EDTA as described, was not examined further, though it is logical to assume that moderate amounts of coloured ions such as nickel, cobalt and chromium^{III} would still interfere in the same way as copper^{II}.

As with cations, the interference of only a selected range of anions was examined. These were nitrate, sulphate, chloride, phosphate, perchlorate and acetate. Only chloride was found to interfere.* It was noticeable, however, that the presence of the anions speeded up colour formation. Thus a thousand-fold excess of nitrate ion, relative to the molar concentration of silver ion, caused a reduction of the necessary standing time from 90 to 30 min. Such large excesses of anion, however, caused slightly low recoveries, and promoted instability of the colour. It was noticeable, also, that a moderate excess of nitrate ion (*ca.* ten-fold) was beneficial, in that it eliminated the opalescence of the solution which had hitherto been present. Consequently the addition of an excess of nitrate ion is recommended as a standard procedure.

DISCUSSION

The proposed method for the determination of silver is considered to be essentially simpler than the standard dithizone and *p*-dimethylaminobenzalrhodanine procedures which have hitherto been used almost exclusively for the determination of trace amounts of silver. There is no danger of precipitation and no necessity for critical adjustment of acidity as with *p*-dimethylaminobenzalrhodanine, nor is it essential to extract and control closely conditions such as temperature, purity of reagents, absence of strong daylight (or fluorescent light), as with dithizone. The calibration curve can be reproduced precisely from day to day, and the silver-Pyrogallol red complex, once formed, maintains an unchanged optical density for several days. Consequently, there is a wider latitude of experimental conditions than with the standard methods for silver. The stability of the silver complex is well illustrated by its resistance to break down by chloride ion. Thus, *once the silver complex has been formed* the addition of an amount of chloride ion theoretically sufficient to precipitate all the silver in it causes no diminution in the intensity of the colour. No shielding of the solution from laboratory light sources or normal day-light is required.

TABLE II. ANALYSIS OF UNKNOWN SOLUTIONS FOR SILVER BY THE PYROGALLOL RED PROCEDURE

Ag^+ supplied, μg	Ag^+ found, μg	Error, %
28·30	31·3	+9·6
42·07	41·3	−1·9
29·99	29·9	−0·3
12·30	13·8	+10·9
47·30	47·0	−0·6
57·40	53·7	−6·9
73·10	71·0	−3·0

Against these attractive features relative to conventional reagents, the Pyrogallol red method is subject to more cationic interference. However, these interferences can in most cases be readily overcome by the addition of an amount of EDTA equivalent

* Chloride interferes by slowing down colour formation.

to the total molar concentration of the foreign ions *e.g.*, Ca, Mg, Zn, Pb, Hg^{II}. The necessary amount is readily determined by complexometric titration, since silver does not interfere with complexometric titrations in acid solution, and is readily masked in alkaline media. None of the common anions interferes except chloride.

Finally, the results of the analyses of a series of unknowns are given in Table II. Precision data were obtained by multiple analyses of a series of solutions containing 32·4 μg of silver ion. These gave an average deviation of 1·3 μg Ag (standard deviation $\pm$ 1·8 μg).

EXPERIMENTAL

Reagents

Silver nitrate, $10^{-4}M$: Prepared by dilution of standard 0·1M silver nitrate solution.

Pyrogallol red, $10^{-4}M$: 10·5 mg of Pyrogallol red (B.D.H. Ltd.) dissolved in 125 ml of absolute ethanol and diluted to 250 ml with distilled water.

Sodium acetate, 20%: 20 g of AnalaR sodium acetate trihydrate dissolved in water and diluted to 100 ml.

Sodium nitrate ca. $10^{-3}M$: 85 g of AnalaR sodium nitrate dissolved and made up to 1 litre with distilled water.

Apparatus

Unicam S.P. 600 Spectrophotometer: Operated from stabilised 12V transformer; 1- and 4-cm cuvettes.

Method

(*a*) *Preparation of calibration curve.* Pipette 1-ml to 10-ml aliquots of $10^{-4}M$ silver nitrate solution into 100-ml standard flasks, add 1 ml of $10^{-3}M$ sodium nitrate and enough distilled water to give a constant volume (*i.e.*, 11 ml). Finally add 0·5 ml of 20% sodium acetate to give a final pH of 7–7·5 and 5 ml of $10^{-4}M$ Pyrogallol red reagent. Do not dilute the solutions at this stage, but allow the colour system to develop for 90 min. Then dilute the contents of each flask to 100 ml and measure the optical density of each solution in a 4-cm cuvette at 390 mμ against a standard containing all the reagents but no silver. Provided that the dilution is carried out after 90 min, the absorption measurements may be made either immediately or after the lapse of several hr.

The graph of optical density against the amount of silver taken is a straight line from 10 to 85 μg of Ag and passes through the origin.

$$1 \text{ ml of } 10^{-4}M \text{ } AgNO_3 \equiv 10{\cdot}8 \text{ } \mu\text{g Ag}.$$

(*b*) *Determinations.* Take an aliquot of the unknown silver solution containing <85 μg of Ag^+ (in 10 ml) in a 100-ml flask, add the necessary amount of EDTA solution (*vide infra*) followed by 1 ml of $10^{-3}M$ sodium nitrate solution and sufficient distilled water to make the volume up to 11 ml. Finally, into this solution, pipette 0·5 ml of 20% sodium acetate and 5 ml of $10^{-4}M$ Pyrogallol red solution. Allow the contents to stand for 90 min *without further dilution.* Lastly dilute the contents to 100 ml and measure the absorbance of the solution against a reagent blank containing no silver, but carried throughout the above processes.

(*c*) *Amount of complexan required.* If the silver solution contains ions which react with Pyrogallol red, take a 5-ml or 10-ml aliquot of this solution in a conical flask, add a small amount of the necessary buffer and indicator (*cf.* Table I), and titrate with an EDTA solution of suitable molarity till the end-point is reached. Note the volume of EDTA required per ml of test solution.

Note: Silver does not react with the great majority of metallochromic indicators which function in solutions of low pH, and its chelate with EDTA is too weak to cause high results. If, however, the ions *e.g.*, Mg, Ca, must be titrated in alkaline solution, then both the indicator and the EDTA should be protected, through the addition of potassium cyanide as a masking agent, against attack by silver ions. This allows the total of (EDTA) titratable ions to be determined.

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Zusammenfassung—Pyrogallolrot kann als Regans zur photometrischen Bestimmung von Silber verwendet werden. Das Reagens formt mit Silber einen gelben Komplex der Zusammensetzung $[Ag_2(C_{19}H_8O_8S)]^{2-}$. Die Farbe ist für wenigstens 24 Stunden beständig. Absorptionsmessung bei 390 mμ zeigten, dass im pH-Bereich 7–7·5 Beer's Gesetz bis hinauf zu 85 μg Silber erfüllt ist. Die Farbe ist unbeeinflusst durch Änderungen in Temperatur und Beleuchtung, wie sie normalerweise im Laboratorium auftreten; keine besondere Reinigung des Reagenses ist nötig. Von den gewöhnlichen Anionen stören lediglich die Halide. Die meisten Kationen stören, doch kann das leicht ausgeschaltet werden, durch Zugabe von ÄDTA in einem zu der anwesenden Kationenmenge äquivalenten Betrag. Diese Menge kann leicht mittels einer seperaten Titration in einem Aliquot der Probe ermittelt werden, ohne vom Silber zu trennen. Die Methode scheint besser reproduzierbar zu sein, als die üblicherweise angewandte Dithizonmethode. Brompyrogallolrot kann in gleicher Weise verwendet werden nur ist die Messung bei etwa 440 mμ durchzuführen.

Résumé—Le rouge de pyrogallol peut être utilisé comme réactif pour le dosage spectrophotométrique des ions argent en solution diluée. Le réactif forme un complexe jaune $[Ag_2(C_{19}H_8O_8S)]^{2-}$ dont la couleur est stable pendant au moins 24 h. Les mesures de la densité optique à 390 mμ montrent que, à pH 7–7,5, la loi de Beer est suivie dans le domaine allant jusqu'à 85 μg d'ions Ag^+. La couleur n'est pas modifiée par les variations normales de température ou d'éclairage du laboratoire, et il n'est pas nécessaire de purifier spécialement les réactifs. Aucun des anions communs ne gêne, sauf les halogénures. La plupart des cations gênent, mais cette interférence est facilement évitée par l'addition d'une quantité d'EDTA équivalente à la concentration molaire totale des autres ions métalliques. Ce total peut être facilement déterminé par un simple titrage sur une portion de la solution sans séparer les ions argent. Cette méthode se présente comme plus reproductible que la méthode standard à la dithizone. Le rouge de bromopyrogallol peut être utilisé de manière analogue, les mesures étant faites à environ 440 mμ.

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PHOTOMETRIC TITRATIONS—III

THE CONSECUTIVE TITRATION OF CALCIUM AND MAGNESIUM

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Summary—The photometric titration of calcium in ammonia-ammonium chloride buffer, pH 10, is studied. Ethyleneglycol-bis(aminoethyl)-tetra-acetic acid is used as titrant and murexide as indicator. This method permits the direct titration of calcium in presence of up to a hundred-fold amount of magnesium. The determination of magnesium can immediately follow in the same solution to a photometric end-point using EDTA as titrant and Eriochrome Black T as indicator. Interferences and their exclusion are discussed.

INTRODUCTION

THE "classical" complexometric determination of calcium and magnesium is based on the use of two aliquots. In the first aliquot calcium is titrated at a very high pH where magnesium is precipitated as the hydroxide. In the second aliquot the sum of the two metals is determined at pH 10. The magnesium content is calculated by difference. This procedure is a significant improvement over the methods available before the introduction of complexometric titrations. However, certain disadvantages and limitations persist and many papers have been published describing attempts to overcome them.

The method of masking magnesium by hydroxide precipitation has some disadvantages. The precipitate will include calcium, thus causing an error which will become intolerably high when a certain Mg:Ca ratio is exceeded. This error may be effectively reduced by adding the complexing agent (EDTA) in excess over the amount of calcium present and then precipitating the magnesium and back-titrating the excess of EDTA in an aliquot of the clear supernate.[1] However, this procedure should be classified strictly as a separation and not as masking. Lott and Cheng[2] were able to decrease the co-precipitation of calcium considerably by the addition of polyvinyl alcohol. Burg and Conaghan[3] reported the same effect with acetylacetone.

Another problem caused by the hydroxide precipitation is the adsorption of the indicator; this was studied in detail by Belcher and coworkers.[4] Here, also, the addition of polyvinyl alcohol or acetylacetone serves as an effective remedy.[2,3]

Despite these improvements, the precipitate still was considered a potential source of trouble and its exclusion seemed desirable. Tichomorova and Simackova[5] performed the titration of calcium at a high pH and avoided the magnesium precipitation by addition of tartrate. For high concentrations of magnesium, considerable amounts of tartrate are necessary for a complete prevention of the precipitation. When applying this method, and using EDTA as the titrant, the present authors found high results for calcium, which is in agreement with Burg and Conaghan,[3] and indicates that some of the magnesium is co-titrated.

When EGTA [ethyleneglycol-bis(aminoethyl)-tetra-acetic acid] was introduced as a titrant for calcium the situation was greatly improved, since the titration was

performed at a pH where magnesium remains in solution without the addition of a masking agent. The logarithms of the stability constants of the calcium and magnesium EGTA complexes are 11.0 and 5.2 respectively.[6] This difference is sufficient for the selective titration of calcium in the presence of magnesium. Excellent results have been obtained employing a potentiometric end-point with the mercury drop electrode on the macro[7] as well as on the ultramicro scale.[8] An indirect end-point using the zinc-Zincon system was developed, which permitted a visual titration.[9,10] Unfortunately, this indicator system is very sensitive to changes in the ammonia concentration thus causing difficulties in its application to practical analyses. Both methods are somewhat restricted because certain important masking agents, in particular cyanide, cannot be used.

Burg and Conaghan[3] proposed a combination of the old and new methods. These investigators titrated calcium at a high pH with EGTA (using Calcon as the indicator) in the presence of tartrate to prevent the precipitation of magnesium. No magnesium was co-titrated under these conditions because of the low stability constant of its EGTA complex. Unfortunately, it was impossible to proceed with an EDTA titration of magnesium (using Erio-T as the indicator) after lowering the pH, because the end-point was very sluggish. Therefore, they titrated the sum of calcium and magnesium in another aliquot and again found the magnesium by difference. The use of aliquots is inconvenient, and presents a serious difficulty when only a small volume of the sample is available. Another difficulty occurs in adjusting the pH to a value as high as 13 when a composite sample is to be analysed and ammonium salts have been introduced during any previous analytical operations. These salts would have to be removed before the calcium titration.

The present authors have attempted, therefore, to find a way to titrate calcium in the presence of magnesium at a lower pH. The pH should be in a range where magnesium is not precipitated, thus avoiding errors arising from occlusion, adsorption or the addition of a masking agent. Furthermore, the magnesium should be titrated in the same solution immediately following the calcium determination after only a change of indicator and titrant.

A method based on a visual end-point detection did not seem feasible for theoretical reasons; hence, attention was directed towards a photometric titration. An indicator unusable in a visual titration because of a sluggish end-point might be used in a photometric titration. Furthermore, the second colour transition in the presence of the first indicator will be more readily detected by the phototitrator than by the observer's eye.

Preliminary experiments showed that of all the indicators investigated murexide was the only one which gave a useful colour change with calcium at pH 10. The colour transition at the end-point at pH 10 was insufficient for a visual indication, but gave well developed titration curves when a phototitrator was used. Murexide has frequently been used in photometric titrations of calcium at higher pH values before the introduction of better indicators.[11,12] To the best of the authors' knowledge, murexide has never been used at pH 10.

The absorption spectra of murexide and the calcium-murexide complex at pH 10 are shown in the lower part of Fig. 1 by curves I and II. Subtracting the two curves gives what may be called the Δ-curve, A, in the upper part of Fig. 1. The Δ-curve shows that the largest difference in the absorbance at the end-point occurs at 490 mμ.

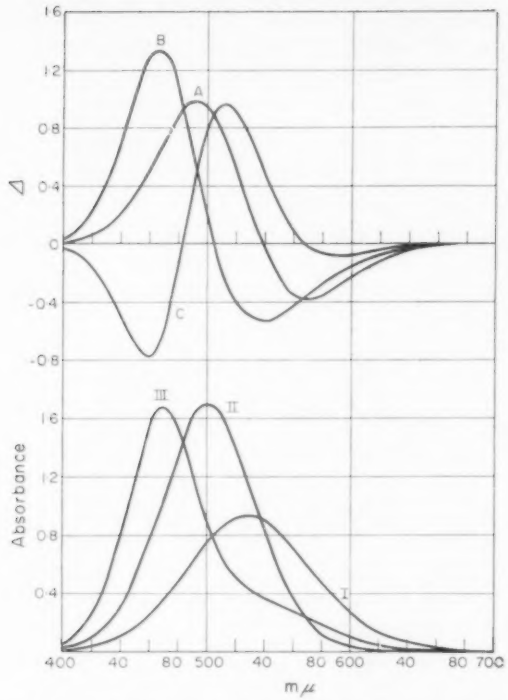

FIG. 1.—Lower part: Spectral curves of I: murexide, II: calcium-murexide complex, III: magnesium-murexide complex. The total concentration of murexide in all three samples was identical. pH 10.
Upper part. A, Δ-curve II minus I (from lower part): B, Δ-curve III minus I (from lower part): C, Δ-curve A minus B (from upper part).

At pH 10, the formation of the magnesium-murexide complex must also be considered. The colour of this rather weak complex is yellow. Its absorption spectrum is shown as curve III in Fig. 1. Therefore, with high magnesium concentrations the colour change will not be to that of free murexide but to the yellow of the magnesium complex. With the phototitrator the situation is a fortunate one, in that at about 505 mμ absorbance curves of the magnesium-murexide complex and the free murexide show an isosbestic point. At this wavelength the response of the phototitrator is independent of the "colour-change" *i.e.*, whether it proceeds to that of murexide or its magnesium complex. This fact is also evident from the Δ-curve, B, which is obtained by subtracting the absorbance curve of the free murexide from the curve of the magnesium-murexide complex. The optimum wavelength for the titration, 505 mμ, can also readily be read from curve C, which is obtained by subtracting curve B from curve A (upper part of Fig. 1.)

Despite the fact that the magnesium-murexide complex is weak, a large excess of magnesium might cause a shift of the equilibrium

$$\text{Ca–Mu} + \text{Mg} \rightleftharpoons \text{Mg–Mu} + \text{Ca} \qquad (1)$$

(omitting charges for simplicity) towards the right to an extent that no useful end-point could be obtained. However, experiments have shown that even with a ratio of

Mg: Ca = 100:1, the break in the titration curve is still sufficiently pronounced to permit a sound extrapolation towards the end-point.

The maximum in the Δ-curve for Erio T and its magnesium complex is at approximately 620 mμ.[6] Murexide does not absorb appreciably at this wavelength, hence there will be no interference when magnesium is titrated after finishing the calcium determination. Preliminary experiments have shown that there is no interference from a small excess of EGTA when magnesium is titrated with EDTA. This excess results from the calcium titration, since some points beyond the end-point are necessary in order to provide an appropriate basis for the extrapolation. Thus the EDTA titration of magnesium can be performed in the same solution immediately following the determination of calcium.

EXPERIMENTAL

Apparatus

All titrations were carried out with the phototitrator described in a previous paper of this series.[13] Rectangular cells with light paths of 1·5 and 3 cm and a capacity of 100–200 ml were used. The absorbance curves were made with a Cary Model 14 Recording Spectrophotometer.

Reagents

Solutions of the metal ions were prepared from appropriate salts. EGTA and EDTA solutions were prepared by dispersing the acids in de-ionised water and adding enough sodium hydroxide to achieve complete dissolution. The solutions were standardised according to well-established chelometric procedures. The indicators murexide and Eriochrome Black T were ground with sodium chloride to a fine powder. All materials used were of reagent grade quality.

Procedure

Exactly measured volumes of the metal ion solutions were pipetted into the titration cell and when necessary were approximately neutralised with sodium hydroxide. Between 5 and 10 ml of buffer (pH 10) were added, and the solution was diluted to about 150 ml. The cell was positioned in the phototitrator and the 508-mμ interference filter was inserted into the filter holder. With this solution as reference 100% transmittance was set on the galvanometer. A spatula tip of ascorbic acid was added to prevent air oxidation of the indicators. Murexide indicator powder was added, and the calcium was titrated with EGTA. The transmittance was recorded and plotted on semi-log graph paper. After the calcium end-point was found, the 622-mμ filter was inserted and Erio T indicator was added. The transmittance was adjusted to about 95% (instead of 100% to provide room for changes through dilution) and the magnesium was titrated with EDTA. The end-points were found at the intersection of the straight lines drawn through the recorded points.

RESULTS AND DISCUSSION

Typical curves are presented in Fig. 2 for the determination of calcium and magnesium alone and for the titration of calcium in the presence of various amounts of magnesium. The end-points in cases of high Mg: Ca ratios can be located better when the curves are replotted in terms of absorbance on linear graph paper with a suitable scale.

Table I shows the very satisfactory precision.

Those metal ions which interfere with the visual titrations of calcium and magnesium of course also interfere with the photometric titration. The same methods of masking can be used successfully with the exception of masking by precipitation. Potassium cyanide was used to mask Co, Ni, Cu, Zn, Cd and Hg. Aluminium was masked by the addition of triethanolamine. Iron was converted into the ferrocyanide complex.[14] When tartrate ion is involved during a masking procedure, care should be taken to avoid too great an excess of it. In the presence of unduly large amounts of tartrate

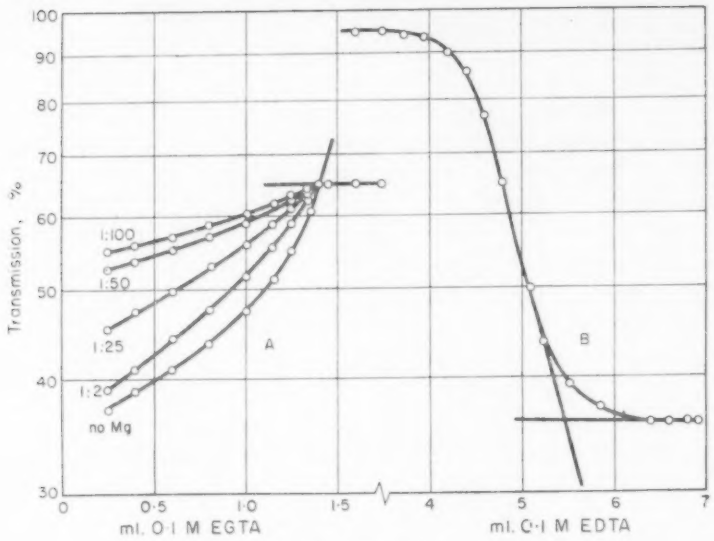

FIG. 2.—Typical titration curves.
A: Calcium titrated with EGTA at pH 10 using murexide as indicator at various ratios of Ca:Mg. 508 mμ.
B: Magnesium titrated with EDTA at pH 10 using Eriochrome Black T as indicator. 622 mμ.

TABLE I. REPRESENTATIVE RESULTS FOR THE TITRATION OF CALCIUM AND MAGNESIUM

$CaCl_2$, 0·1*M*		Mg: Ca ratio	$Mg(NO_3)_2$, 0·1*M*	
Taken, ml	Found, ml		Taken, ml	Found, ml
2·95	2·96	—	none	
5·23	5·22	—	none	
9·45	9·50	—	none	
none		—	2·65	2·68
none		—	3·66	3·61
none		—	4·38	4·41
3·60	3·65	1·7:1	6·02	6·02
4·29	4·29	0·7:1	3·07	3·06
6·43	6·42	0·15:1	0·94	0·98
1·13	1·15	22:1	25	not determined
1·24	1·17	40:1	50	not determined
1·00	1·04	100:1	100	not determined
1·51	1·55	132:1	100 (0·2*M* Mg)	not determined

a drift of the galvanometer pointer was observed for which, at the present time no satisfactory explanation can be given.

It is essential to protect both indicators from air oxidation (which manifests itself *via* a drift of the galvanometer) by maintaining a sufficient concentration of ascorbic acid in the titration solution. If the titration is extended over a longer period of time, further additions of ascorbic acid during the titration are recommended.

It is of advantage to keep the solutions reasonably free of carbon dioxide, otherwise a precipitate of calcium carbonate may form. This precipitate will disappear

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during the course of the titration. It is, however, important to proceed very slowly especially near the end-point, because the dissolution is a slow process. No false results are obtained when working with slightly turbid solutions when the rate of titration is reduced appropriately.

The new method was practically evaluated by the analysis of an NBS sample "Burned Magnesite No. 104". The sample was dissolved in hydrochloric acid and filtered into a volumetric flask. An aliquot of the solution was taken, the iron and aluminium masked with cyanide and triethanolamine. A turbidity which occurred during the process was filtered off, and the calcium was titrated with EGTA in the manner described above.

A determination in triplicate gave the following values: 3·34, 3·29 and 3·52%. The average, 3·38%, compares favourably with the certified value of 3·35% of CaO.

Acknowledgement—This work was performed under a grant from the National Science Foundation. Permission to use their Cary Model 14 Spectrophotometer was given by the Coca-Cola Co., Atlanta, Ga., U.S.A. The National Bureau of Standards provided the magnesite sample. These aids are gratefully acknowledged.

Zusammenfassung—Die photometrische Titration von Calcium in Ammoniak-Ammoniumchlorid-Puffer pH 10 wird beschrieben. Äthylenglycol- bis(aminoäthyl) tetraessigsäure ist das Titrationsmittel und Murexid der Indicator. Die Methode gestattet die direkte Bestimmung von Calcium in Gegenwart von bis zur hundertfachen Menge Magnesium. Die Bestimmung des Magnesiums kann unmittelbar angeschlossen werden, wobei mit ÄDTE titriert wird und Eriochromschwarz T als Indicator dient. Störungen werden untersucht und über ihre Ausschaltung wird berichtet.

Résumé—Les auteurs ont étudié le dosage photométrique du calcium en tampon ammoniaque-chlorure d'ammonium à pH 10. L'acide éthylène glycolbis (aminoéthyl) tétracétique est utilisé comme agent titrant et la murexide comme indicateur. Cette méthode permet le titrage direct du calcium en présence de plus de cent fois plus de magnésium. Le dosage du magnésium peut suivre immédiatement dans la même solution le point équivalent étant déterminé par photométrie en utilisant l'EDTA comme agent titrant et le noir ériochrome T comme indicateur. Les interférences et leur élimination sont discutées.

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DETERMINATION OF ALKALI SULPHIDES BY DIRECT TITRATION

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Summary—A new titrimetric method has been developed for the determination of sulphides with cadmium acetate standard solutions and dead-stop indication. The determination must be carried out in a medium buffered by sodium acetate. The determination is not interfered with by sulphur oxides, nitrites, but it is affected by hydroxide and cyanide ions.

THE simple and rapid iodometric method cannot be applied to the determination of the sulphide content of sodium sulphide, because sodium sulphide is decomposed into various sulphur acids through time; the presence of these interferes with the determination. The determination is sometimes made by precipitating the sulphide with cadmium acetate, and titrating the sulphide precipitate iodometrically after filtration.[1] When the necessary precautions are taken, the method is fairly accurate, but lengthy.

It was necessary therefore to develop a rapid direct titration method.

The method was developed on the basis of the property of sulphide of forming very insoluble precipitates with many cations. For precipitation-titration investigations silver and cadmium ions were selected; the end-points were determined potentiometrically. Employing sulphide solutions of high purity, the titration can be carried out with either cation and a sudden potential change of 1000 or 300 mV respectively, can be measured at the end-point.

For the results obtained with various standard solutions, a constant deviation of 1–2% (corresponding to the solubility product) can be maintained.

Should sulphur acids (sulphite, thiosulphate) or chloride be present in addition to sulphide, the determination can be made only with cadmium standard solution, since the silver ions will react with sulphur acids and chloride.

It has also been investigated whether the end-point of the titration with cadmium may be indicated by the very elegant dead-stop method. On the basis of the promising initial results, a dead-stop indication method for the determination of sulphide with cadmium acetate standard solution was developed.

EXPERIMENTAL

Standard solution

Dissolve 26·65 g of cadmium acetate, $Cd(CH_3COO)_2 \cdot 2H_2O$, and 5 g of concentrated acetic acid in 1000 ml. The cadmium acetate solution is standardised, by the present method against a sulphide solution, the concentration of which has been determined.

The concentration of the sulphide solution is determined by precipitating the sulphide by excess cadmium acetate, filtering, transferring the cadmium sulphide precipitate together with the filter paper to a hydrochloric acid—iodine standard solution, and titrating the excess iodine by thiosulphate standard solution. The sulphide concentration is calculated from the iodine consumption.

Procedure

Transfer 20 ml (20–50 mg of S) from the approximately neutral solution under investigation to a beaker, dilute by boiled distilled water to *ca.* 50 ml, and add approximately 1 g of crystallised sodium acetate. Employing a galvanometer of $1{\cdot}5$–$4{\cdot}0 \times 10^{-8}$ A sensitivity for 50–100 mV potential, titrate the solution with a $0{\cdot}1M$ cadmium acetate standard solution, using dead-stop indication. During titration, the current intensity decreases continuously, but increases suddenly at the end-point.

The accuracy of the method is $\pm 0{\cdot}2\%$. Results of measurements are shown in Table I.

TABLE I.

No.	Weight of sample, *mg* of S^{--}	Weight found, *mg* of S^{--}	Deviation	
			mg	%
1	29·70	29·67	−0·03	−0·1
2		29·65	−0·05	−0·2
3	26·00	25·98	−0·01	−0·1
4		25·97	−0·03	−0·1
5	31·20	31·26	+0·06	+0·2
6	52·0	51·97	−0·03	−0·1
7		52·04	+0·04	+0·1

DISCUSSION

At the beginning of the titration, the galvanometer needle must be near the end of the scale, since the current intensity decreases continuously during titration, but shows a sudden increase only at the end-point (Fig. 1.) This increase in intensity is,

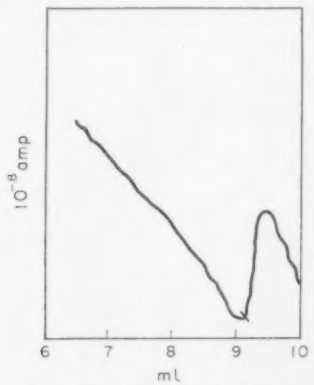

Fig 1. Titration curve of sulphide ion

however, only transitory, since it decreases again upon addition of excess standard solution. It is probable that the increase in intensity of the current is brought about by the system consisting of dissolved cadmium sulphide and cadmium acetate. The dissociation of the cadmium sulphide is slowly suppressed by the excess cadmium acetate, resulting in gradual decrease of the intensity.

The determination can only be carried out below pH 7, because at higher pH values there is no sudden change at the equivalence-point. The reason for this is the reaction of hydroxyl ions with cadmium, which occurs to a greater extent when the hydroxyl is bound to ammonium ion. In neutral and acidic media, ammonium ion does not interfere with the reaction.

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In strongly acidic medium, loss of sulphide from the solution is considerable. Taking into account the above considerations, a sodium acetate medium ensuring a pH of *ca.* 6–6·4 was selected for the measurement.

The determination is interfered with by hydroxyl and cyanide. No trouble is caused by sulphur acids, nitrite, chloride, *etc.*

Acknowledgement—I take this opportunity to express my thanks to my co-worker, Mrs. Rozsa B Doszpod for her help in carrying out the measurements.

Zusammenfassung—Eine neue, titrimetrische Methode zur Bestimmung von Sulfid mittels Cadmiumazetatlösung und "dead stop"-Endpunkt wurde ausgearbeitet. Die Titration muss in einem mit Natriumazetat gepufferten Medium durchgeführt werden. Die Bestimmung wird nicht beeinflusst durch die Anwesenheit von Schwefeldioxyd oder Nitrit, wird jedoch durch Hydroxyd- und Cyanionen gestört.

Résumé—L'auteur a mis au point une nouvelle méthode titrimétrique de dosage des sulfures par une solution étalon d'acétate de cadmium et détermination du point équivalent par dead stop. Le dosage peut être réalisé en milieu tamponné par de l'acétate de sodium. Les oxydes de soufre ou les nitrites ne gènent pas le dosage, mais les ions hydroxyle et cyanure le pertubent.

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5-AMINO-2-BENZIMIDAZOLETHIOL AS AN ANALYTICAL REAGENT—I

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

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Summary—The orange coloured complex formed by palladium[II] with 5-amino-2-benzimidazolethiol in the pH range 2–4 forms the basis of a very sensitive colorimetric method for the determination of trace amounts of the metal. The complex shows maximum absorption at 390 mμ, where the reagent has negligible absorption, and it obeys Beer's law from 1 to 8 ppm of palladium[II], the optimum range being 2–7 ppm where the percentage relative error per 1% absolute photometric error is 2·95. The sensitivity of the reaction is 0·008 μg/cm^2. Most of the common cations and anions are without effect on the complex. The interferences of some of the platinum metals are avoided by developing the complex in the cold and using EDTA (disodium salt) as a masking agent. A composition study by the molar ratio method shows that at pH 3·42 the solution contains both 1:1 and 1:2 complexes, the dissociation constant of the latter being $1{\cdot}32 \times 10^{-11}$. However, above pH 5·5 incipient precipitation of the orange-red palladium complex occurs, and the precipitation is quantitative above pH 10. The analysis of this precipitate shows a ratio of 1:2 between the metal and the reagent.

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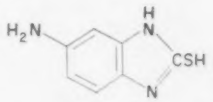
INTRODUCTION

5-AMINO-2-BENZIMIDAZOLETHIOL (I) has been found to be a sensitive reagent for the



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spectrophotometric determination of palladium in aqueous solution. Since no mention of the use of the reagent in analytical processes is found in the literature, a systematic study of its reactions with noble and common metals has been undertaken. This showed that with the exception of iron the reagent was almost unreactive towards common metals. It reacts, however, with some platinum metals and silver, but under controlled conditions it is highly selective for palladium[II]. The orange coloured palladium complex is soluble below pH 5.5 and shows maximum absorption at 390–400 mμ where the reagent absorption is negligible. The reagent precipitates palladium quantitatively above pH 10, suggesting the possibility of its use as a gravimetric reagent.

EXPERIMENTAL

Apparatus

Wavelength-transmittance curves of the complex were obtained with a Beckman DK1 recording Spectrophotometer, and absorbances of other solutions were measured with a Beckman DU Spectrophotometer. In all cases, 1·00-cm silica cells were used.

A Beckman model G pH meter was employed for all pH determinations.

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Reagents

Standard palladium solution: A standard solution of palladium was prepared by dissolving 1 g of palladous chloride in hot water containing 10 ml of concentrated HCl and diluting to 500 ml. This solution was standardised gravimetrically by the α-picolinic acid method.[1]

5-Amino-2-benzimidazolethiol solution: A 0·5% solution of the reagent was prepared by suspending 0·5 g of the recrystallised reagent (m.p. 245°, Eastman Organic Chemicals Department, U.S.A.) in 100 ml of water, and dissolving by the dropwise addition of 6*N* acetic acid and stirring.

Buffer solutions: Buffer solutions of pH range 3·42–5·89 were prepared by mixing 0·2*N* acetic acid with 0·2*N* sodium acetate in different proportions.[2]

Other reagents: Solutions of other platinum metals and common ions were prepared as described in a previous paper.[3]

Reactions of 5-amino-2-benzimidazolethiol with cations

Simple qualitative tests of the reagent with diverse metal ions were carried out in weak acid medium (pH 2–5) both in the cold and hot solutions. It was found that the reagent does not react with common ions like Zn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, As^{+3}, Cu^{+2}, Cr^{+3}, Al^{+3}, Co^{+2} or Ni^{+2}. With Fe^{+3} it gives a yellow precipitate. The reactions of the reagent with noble and platinum metals are listed in Table I.

TABLE I.

Metal	Taken as	Reaction in cold solution	Reaction in hot solution
Os^{VIII}	OsO_4	Purple colour but no precipitate	As in cold solution
Pt^{IV}	H_2PtCl_6	Yellow colour but no precipitate	As in cold solution
Rh^{III}	$RhCl_3$	No change	Orange colour
Ru^{III}	$RuCl_3$	No change	As in cold solution
Pd^{II}	$PdCl_2$	Intense orange colour	As in cold solution
Ir^{IV}	Na_2IrCl_6	No change	As in cold solution
Au^{III}	$AuCl_3$	No change	As in cold solution
Ag^{I}	$AgNO_3$	No change	White precipitate

Colorimetric determination of palladium with 5-amino-2-benzimidazolethiol

Recommended procedure: Five ml of 0·5% reagent solution were added to the $palladium^{II}$ solution taken in a 25-ml volumetric flask, and the volume was made up with buffer solution of pH 3·42. After allowing to stand for 35 min at room temperature, the absorbance was measured against a reagent blank prepared identically without palladium.

RESULTS AND DISCUSSION

Spectral curve

The wavelength-transmittance curve of the complex (Fig. 1) shows that the maximum absorption takes place in the region 390–400 mμ, where the reagent has negligible absorption.

Effects of pH, reagent concentration and time

Between pH 2 and 4 the absorbance of the complex remains constant at 390 mμ. At lower or higher pH values the absorbance increases slightly.

For 4 ppm of palladium, 5 ml of 0.5% reagent are necessary for full development of the colour. Greater amounts of reagent do not increase the absorbance if the measurements are carried out against a reagent blank at 390 mμ.

The colour begins to develop instantaneously at room temperature when the reagent is added to a palladium solution at pH 2–4, and a constant absorbance value

is obtained after standing for 35 minutes and measuring at 390 mμ. The colour is stable for 24 hours.

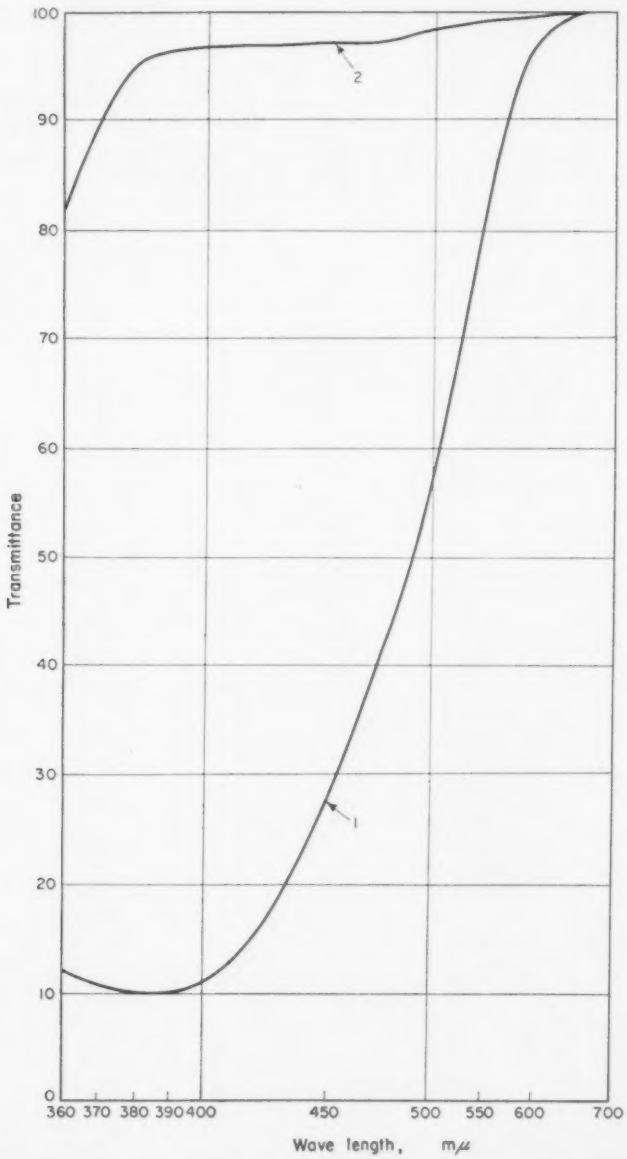

FIG. 1.—Wavelength-transmittance curves of 5-amino-2-benzimidazolethiol and its palladium^{II} complex at pH 3·42.
Curve 1: 8 ppm of palladium^{II} + 5 ml of 0·5% reagent solution.
Curve 2: 5 ml of 0·5% reagent solution diluted to 25 ml with buffer, pH 3·42

Beer's law, optimum range and accuracy

The colour complex obeys Beer's law for a palladium^{II} concentration of 1 to 8 ppm (Fig. 2). Ringbom's[4] curve (Fig. 3), as obtained by plotting percentage absorptancy

(*i.e.* 100 — % transmittance) versus log concentration, shows that the optimum concentration range is between 2 and 7 ppm where the percentage relative error per 1% absolute photometric error, as evaluated by Ayres' equation,[5] is 2·95.

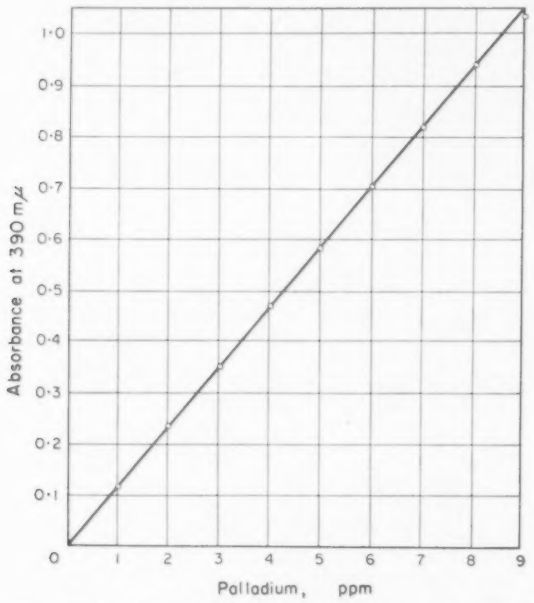

FIG. 2.—Beer's law plot for the palladium[II] complex at pH 3·42.

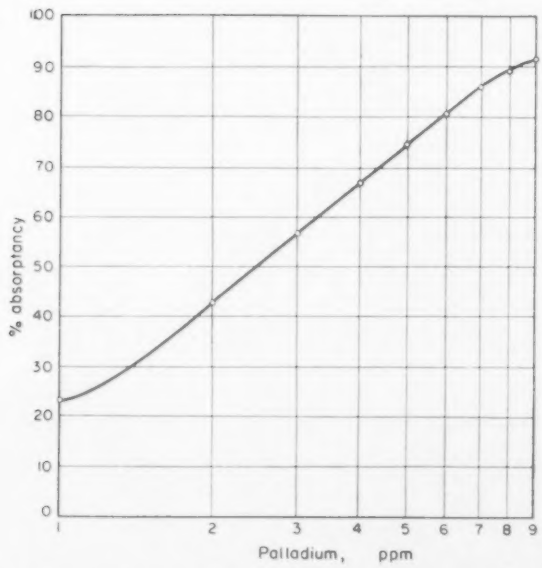

FIG. 3.—Calibration curve for palladium[II] complex at 390 mμ, pH 3·42.

Sensitivity

Sandell's[6] spectrophotometric sensitivity, as calculated from Beer's law data, is 0·008 μg/cm^2, and the molecular extinction coefficient is $5{\cdot}46 \times 10^4$. This is calculated from the equation: Molecular extinction coefficient $= \frac{M}{S}$ where M = mol. wt. in g. of the 1:2 complex, S = Sandell's sensitivity.[6]

Effect of diverse ions

The effect of diverse ions on the complex was studied by adding different amounts of the ionic species to the palladium^{II} solution and then developing the colour exactly as outlined under *Recommended Procedure*. An increase or decrease of 0·005 unit in the absorbance value was considered to be an interference. It was found that the disodium salt of ethylenediaminetetra-acetic acid (EDTA) could increase the tolerance limits of a number of ions. The tolerance limits of various ions for 4 ppm of palladium^{II}, with and without EDTA (disodium salt), are given in Table II.

TABLE II.

Ion	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*	Ion	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*
Ru^{+3}	—	4	Zn^{+2}	—	16
Ru^{+3}	32	12	Zn^{+2}	32	32
Rh^{+3}	—	8	Cd^{+2}	—	40
Ir^{+3}	—	8	As^{+3}	—	40
Ir^{+3}	32	16	Pb^{+2}	—	40
Au^{+3}	—	8	Mn^{+2}	—	16
Cu^{+2}	—	4	Mn^{+2}	32	32
Cu^{+2}	32	8	UO_2^{+2}	—	64
Ni^{+2}	—	8	MoO_4^{-2}	—	40
Ni^{+2}	32	16	WO_4^{-2}	—	40
Co^{+2}	—	40	Th^{+4}	—	40
Al^{+3}	—	40	Zr^{+4}	—	40
Cr^{+3}	—	32	Cl^{-1}	—	>200
NO_3^{-1}	—	>200	SO_4^{-2}	—	>200

Platinum^{IV} interferes even in the presence of EDTA (disodium salt). Osmium should be separated from palladium as osmic acid by nitric acid distillation[6] in order to avoid its interference.

Composition study of the palladium complex

The composition of the complex in solution was studied by the molar ratio method of Yoe and Jones.[7] For this method, solutions were prepared at pH 3·42 in such a way that the palladium^{II} concentration remained constant but the ratio of the moles of reagent to the moles of palladium varied from 0·25 to 4·0. The absorbances of these solutions were measured at 390 mμ against a water blank. The results, as represented in Fig. 4, show two breaks corresponding to 1:1 and 1:2 complex-formation between the metal and the reagent. Evidently at the lower reagent concentration

a 1:1 complex is formed and this changes to a 1:2 complex when the reagent is in excess.

The palladium-reagent complex was found to be precipitated above pH 5·5, but the precipitation was quantitative only above pH 10. The palladium complex precipitated both at pH 6 and at pH 10 was filtered through a sintered-glass crucible, washed thoroughly with hot water and dried at 110°. An accurately weighed amount of each dried portion was then decomposed by wet digestion with nitric acid-perchloric acid mixture and the palladium was determined by the α-picolinic acid method.[1]

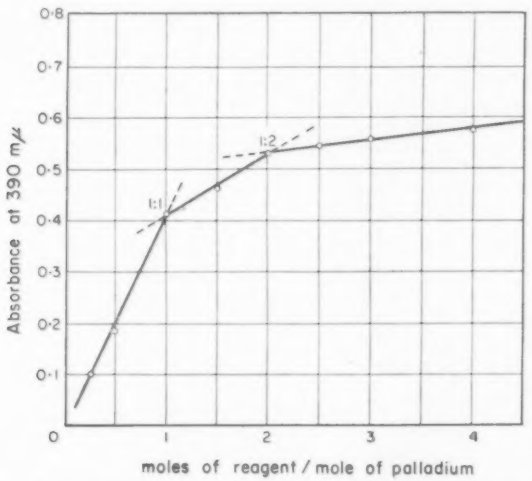

FIG. 4.—Determination of the ratio of palladium to reagent by molar ratio method. Palladium^{II} concn. = $6{\cdot}78 \times 10^{-5}M$; reagent concn. varied.

The complex was found to have the composition $Pd(C_7H_7N_3S)_2$ (% Pd calc., 24·41; found 24·39 at pH 6, 24·40 at pH 10).

Dissociation constant

From the absorption data of Fig. 4, the dissociation constant of the 1:2 palladium complex in solution was calculated by employing the equations $K = (\alpha C)(n\alpha C)^n / C(1 - \alpha)$ and $\alpha = (E_m - E_s)/E_m$ of Harvey and Manning[8] and the value was found to be $1{\cdot}32 \times 10^{-11}$ at room temperature.

Comparison of 5-amino-2-benzimidazolethiol with other colorimetric organic reagents for palladium

Table III illustrates the organic reagents that are available for the colorimetric determination of palladium in the optimum concentration range of 0·5 to 10·0 ppm. Though some of these reagents are fairly sensitive in developing a colour, almost all suffer from non-specificity for palladium, so that in all cases prior separation of palladium is essential. The advantage of using 5-amino-2-benzimidazolethiol is that it does not react with common metals, and under controlled conditions it can be made highly selective for palladium. It also compares favourably with other reagents in sensitivity and in the concentration range of palladium with low percentage relative error.

TABLE III.

Reagent	Wavelength for maximum absorption, *mμ*	Optimum concn. range, *ppm*	Interferences	Reference
p-Nitrosodiphenylamine	510–525	0·5 to 3·0	Ag, Au, and large amounts of Pt metals	9, 10
1-Nitroso-2-naphthol	420	0·5 to 5·0	Ni, Fe, Co	11
2-Nitroso-1-naphthol	370	1·0 to 5·0	EDTA masks the interferences of Cu, Cr, Ni, Co, Fe. No interference from other Pt metals	12
α-Furildioxime	420	1·2 to 4·8	Ru, Rh, Ir, Pt, Au,	13
3-Hydroxy-1-*p*-sulphonato-phenyl-3-phenyltriazine	413	0·2 to 6·0	Can tolerate very small amounts of Fe^{III}, Rh, Ir and Pt	14
Bismuthiol I	400–410	0·8 to 8·0 (Beer's law range)	Pt, Au, Cu, Cr, Fe, Hg, Ag, Tl, U	15
Bismuthiol II	410–430	0·8 to 8·0 (Beer's law range)	Pt, Au, Cu, Cr, Fe, Hg, Ag, Tl, U	16
Phenyl-1-pyridyl ketoxime	410, 340	2·0 to 10·0	Au, phosphate, cyanide. EDTA masks interferences of a number of ions	17
Quinoxaline-2,3-dithiol	548	0·4 to 3·0	Pt, Os, Fe^{III}, Co, Ni	18
Thiomalic acid	350	1·1 to 2·6	Ni, Co do not interfere. Fe, Cu, Ru, Os, Au	19
N,N′-Bis(3-dimethylamino propyl)dithiooxamide	427	1·6 to 5·7	Relatively high concn. of Pt, Rh, Ir, Au, Co, Ni, can be tolerated	20
5-Amino-2-benzimidazolethiol	390	2·0 to 7·0	Rh, Ir, Au, Ni, Co and other common metals do not interfere. Larger amounts of Ru, Ir, Cu, Ni, Zn, Mn can be tolerated by using EDTA as a masking agent	Present work

Acknowledgement—The author expresses his deep gratitude to Dr. Philip W. West, Boyd Professor of Chemistry, for providing laboratory facilities.

Zusammenfassung—Palladium(II) gibt mit 5-Amino-2-benzimidazolthiol im pH-Bereich 2–4 eine orange Färbung, was zur sehr empfindlichen Bestimmung von Spurenmengen herangezogen werden kann. Der gefärbte Komplex zeigt ein Absorptionsmaximum bei 390 mμ, wo das Reagens eine zu vernachlässigende Absorption aufweist. Beer's Gesetz wird für Mengen von 1–8 ppm erfüllt, der optimale Bereich ist 2–7 ppm, wobei der relative Fehler 2·95 beträgt (für einen absoluten photometrischen Fehler von 1%). Störungen durch einige Platinmetall kann vermieden werden, indem die Farbe in der Kälte entwickelt und ÄDTE als Maskierungsmittel zugesetzt wird. Die Empfindlichkeit der Reaktion ist 0·008 μg/cm². Bei pH 3·42 lassen sich ein 1:1 und ein 1:2 Komplex nachweisen. Die Dissoziationskonstante des letzteren beträgt $1{\cdot}32 \times 10^{-11}$. Bei pH 5·5 beginnt der orangegelbe

Komplex auszufallen. Die Fällung ist bei pH 10 quantitativ. Der Niederschlag zeigt eine Zusammensetzung Pd:Reagens = 1:2.

Résumé—La couleur orangée formée par le palladium et le 5-amino-2-benzimidazolethiol dans un domaine de pH 2–4 est à la base d'une méthode colorimétrique très sensible de dosage de traces du métal. Le complexe coloré a un maximum d'absorption à 390 mμ, longueur d'onde à laquelle le réactif a une absorption négligeable; il suit la loi de Beer de 1 à 8 p.p.m. de palladium (II), le domaine de concentration le meilleur étant 2–7 p.p.m., pour lequel l'erreur relative, pour une erreur photométrique absolue de 1%, est de 2,95%. La sensibilité de la réaction est 0,008 μg/cm². La plupart des anions et des cations communs sont sans effet sur le complexe coloré. Les interférences des métaux de la mine du platine sont évitées en formant le complexe à froid et en utilisant l'EDTA (sel disodique) comme agent complexant. Les études de la composition du complexe par la méthode du rapport molaire montrent que, à pH 3,42, la solution contient les complexes 1/1 et 1/2, la constante de dissociation de ce dernier étant $1{,}32 \cdot 10^{-11}$. Cependant, à pH supérieur à 5,5, la précipitation du complexe rouge orange palladium-réactif commence; elle devient complètement quantitative à pH supérieur à 10. L'analyse du précipité montre un rapport métal/réactif de 1/2.

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SPECTROPHOTOMETRIC AND POTENTIOMETRIC STUDIES ON THE COMPOSITION OF IRON COMPLEXES OF POTASSIUM MOLYBDO- AND MOLYBDICYANIDE

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Summary—Iron^{III} forms a soluble complex with potassium molybdocyanide. An instantaneous blue colour is produced when ferric chloride is added to a solution of potassium molybdocyanide. The composition of the complex was determined by the method of continuous variation and by the slope ratio method, which indicated the existence of the complex $KFe^{III}Mo^{IV}(CN)_8$. The formation constant of the complex was found to be $1{\cdot}37 \times 10^4$ and the free energy of formation works out to be $-5{\cdot}57$ Kcals at 20°. Ferric sulphate also gives a blue complex with potassium molybdicyanide. Its composition has been studied potentiometrically using the $Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ couple at a bright platinum electrode; it was found to be $K\,Fe^{II}Mo^{V}(CN)_8$.

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SOLUBLE complexes of heavy metal molybdocyanides are not reported in the literature. We, for the first time, obtained a Cr^{III} complex of this type by the interaction of chromium^{III} chloride and potassium molybdocyanide, and assigned the formula $KCr^{III}Mo^{IV}(CN)_8$ to the red compound[1,2] thus obtained. Other soluble complexes of this series were obtained by the interaction of Fe^{III} with potassium molybdocyanide and Fe^{II} with potassium molybdocyanide. This communication deals with the composition of these complexes as indicated by physico-chemical methods of examination.

Preliminary experiments on the interaction of iron^{III} chloride and iron^{II} sulphate with potassium molybdocyanide and potassium molybdicyanide respectively gave evidence of similar type of colour changes. Thus it was observed that with excess of iron^{III} or iron^{II} ions, a blue solution was obtained, but with excess of molybdo- or molybdicyanide a greenish-blue solution is obtained. Since the reaction appeared to be analogous to that observed in the formation of "iron blues", it was thought worthwhile to elucidate the nature and composition of the complex or complexes formed, using various physico-chemical methods.

The composition of the complex formed by the interaction of ferric chloride and potassium molybdocyanide could not be studied satisfactorily by conductometric, potentiometric or amperometric titration methods. Interestingly enough this complex was found to be reducible at the dropping mercury electrode, giving a typical polarographic wave, but the polarographic method[3] could not be successfully employed either in view of the fact that the complex became unstable on coming in contact with the mercury drops (a slight turbidity, followed by precipitation in the polarographic cell, was observed). The spectrophotometric method was, however, found useful in determining the composition and stability of the complex. This method was also tried for investigating the complex formed by the interaction of ferric sulphate and potassium molybdicyanide, but reliable information could not be obtained since $K_3Mo(CN)_8$ was appreciably decomposed by the light from the tungsten lamp of the

spectrophotometer. Several electrometric methods were then tried and it was found that very satisfactory results could be realised by a potentiometric method, using a $Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ couple at a bright platinum electrode.

EXPERIMENTAL

Reagents

Ferric chloride (AnalaR) and *ferrous sulphate* (recrystallised three times) were dissolved in doubly distilled water and the strengths of the solutions were determined by the usual methods. *Potassium molybdocyanide* was prepared by the method recommended by Fieser[4] and the strength of the solution was determined by titrating potentiometrically against $KMnO_4$ solution. Kolthoff's method[5] was used for obtaining *potassium molybdicyanide*. The strength of the solution was also determined potentiometrically using potassium ferrocyanide.

Apparatus

A Beckman DU spectrophotometer with 1-cm Corex cells and a tungsten lamp as the light source was used for optical density measurements.

PROCEDURES

In order to determine the number of complexes formed by the interaction of ferric chloride and potassium molybdocyanide, the method of Vosburgh and Cooper[6] was followed. The reactants were mixed in different proportions and the optical density was measured at different wavelengths ranging from 360 mμ to 1000 mμ. All the mixtures gave a maximum at 840 mμ showing thereby the formation of only one complex (Fig. 1).

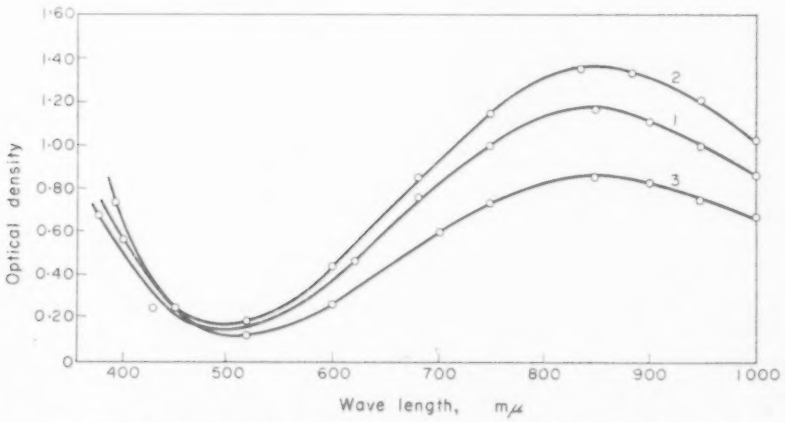

FIG. 1.—$FeCl_3$ and $K_4Mo(CN)_8$ mixed in the proportions (1) 2:1, (2) 1:1, and (3) 1:2. Concentration of the reactants, $3{\cdot}3 \times 10^{-3}M$.

Job's method[7] of continuous variation was followed for determining the composition of ferric molybdocyanide. Solutions of ferric chloride and potassium molybdocyanide of three different concentrations, *viz.*, $4 \times 10^{-3}M$, $2 \times 10^{-3}M$ and $1{\cdot}25 \times 10^{-3}M$, were mixed according to the method of continuous variation, and O.D. was measured at 840 mμ after 10 min of mixing. Ferric chloride and potassium molybdocyanide at these concentrations had a negligibly small absorption at 840 mμ. The optical densities of the solutions were plotted against the ratio $[Fe^{3+}]/[Fe^{3+}] + [Mo(CN)_8^{4-}]$. The results are depicted in Fig. 2.

The results were further confirmed by the slope ratio method.[8] Two sets of experiments were performed. In the first set the concentration of potassium molybdocyanide was kept constant and that of ferric chloride was varied; in the other set the mixing was done in the reverse order. The results are given in Fig. 3. The slope was determined over the straight line portion of the curve.

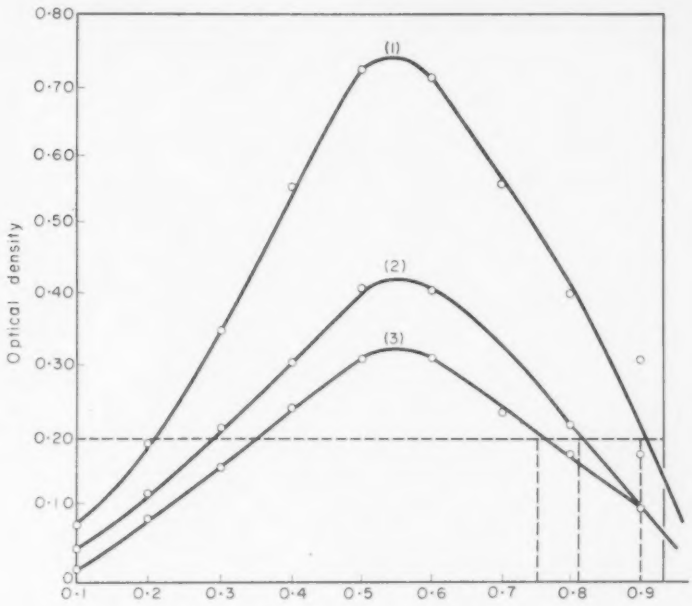

FIG. 2.
The ratio $Fe^{3+}/Fe^{3+} + Mo(CN)_8^{3-}$. Concentrations of the reactants, (1) $4 \times 10^{-3}M$, (2) $2 \times 10^{-3}M$ and (3) $1{\cdot}25 \times 10^{-3}M$.

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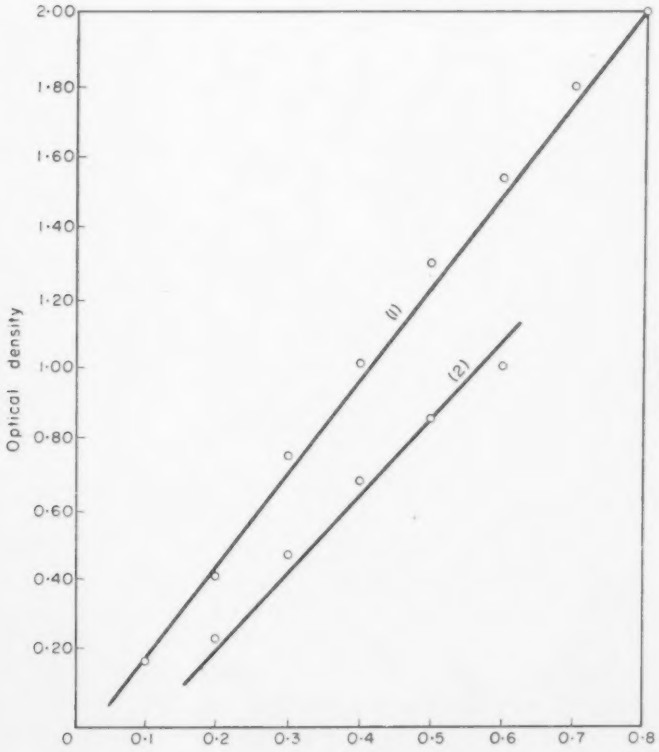

FIG. 3.
Slope ratio method.
(1) Concentration of $K_4Mo(CN)_8$ constant, $1{\cdot}66 \times 10^{-3}M$. Concentration of $FeCl_3$ varied, $2 \times 10^{-2}M$.
(2) Concentration of $FeCl_3$ constant, $1{\cdot}66 \times 10^{-3}M$.
Concentration of $K_4Mo(CN)_8$ varied, $2 \times 10^{-2}M$.

Potentiometric titrations between ferrous sulphate and potassium molybdicyanide were carried out using a Tinsley Vernier potentiometer (type 33873); the indicator electrode [$Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ couple] was obtained by dipping a bright platinum electrode in the solution of potassium molybdicyanide containing a little potassium molybdocyanide. The titrations at three different concentrations of molybdicyanide solution, *viz.*, 0·03*M*, 0·02*M* and 0·02*M*, were performed for determining the composition of ferrous molybdicyanide. In the cell fitted with the indicator electrode and the saturated calomel electrode, 10 ml of the molybdicyanide solution were taken and ferrous sulphate (0·1*M*) was added from the burette. The curves are shown in Fig. 4. Reverse titrations with ferrous sulphate in the cell were not successful. The experiments were performed in a dark room and the vessels were wrapped with black paper to avoid the decomposition of potassium molybdicyanide by light.

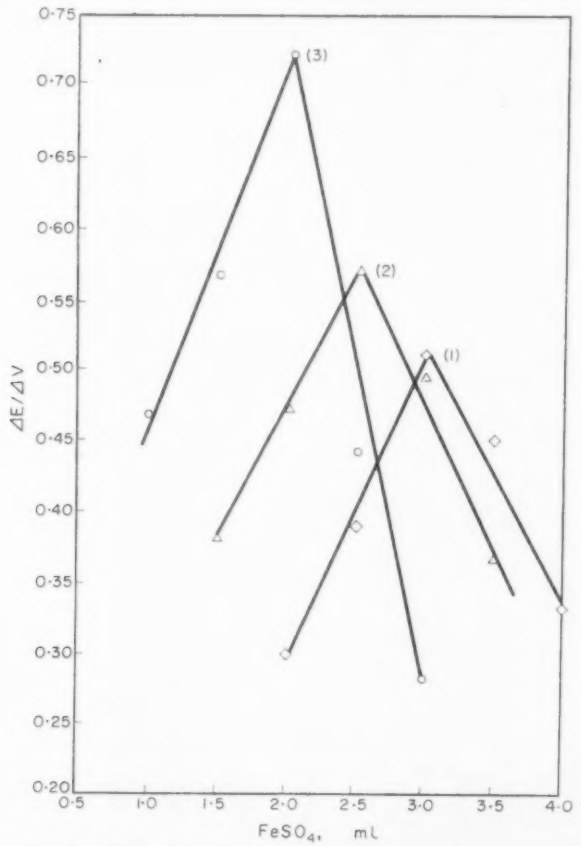

FIG. 4.—Determination of end-point in potentiometric titration. 10 ml of $K_3Mo(CN)_8$ of concentration (1) 0·03*M*, (2) 0·025*M*, and (3) 0·020*M* versus 0·1*M* $FeSO_4$.

DISCUSSION

Several authors, including Davidson,[9] have extensively investigated the nature of the reaction between ferrous chloride and potassium ferrocyanide and the composition of the complex. When iron^{III} ions are added to an equimolecular quantity of ferrocyanide ions, a redox equilibrium sets in with the result that the iron^{III} ions are almost completely reduced to iron^{II} ions by the ferrocyanide ions, which, in turn, are simultaneously oxidised to ferricyanide ions. The possibility of such a redox

equilibrium, existing in the case of the ferric chloride-potassium molybdocyanide reaction appears to be remote, since the equilibrium constant value,

$$K298 = \frac{[Fe^{3+}][Mo(CN)_8^{4-}]}{[Fe^{2+}][Mo(CN)_8^{3-}]} = 10{\cdot}4,$$

$$(Fe^{2+} \rightleftharpoons Fe^{3+} + e,\ E_0 = -0{\cdot}76;$$

$$Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e,\ E_0 = -0{\cdot}82)$$

is quite low when compared to the ferric chloride-potassium ferrocyanide reaction ($K298 = 1{\cdot}215 \times 10^5$). Thus on theoretical grounds it could be inferred that the complexes formed by the interaction of ferric chloride and potassium molybdocyanide, and between ferrous sulphate and potassium molybdicyanide, could not be one and the same and unlike "iron blues" would have different compositions.

The combining ratio of 1:1 for Fe^{3+} to $Mo(CN)_8^{4-}$ is obtained both by the continuous variation and slope ratio methods (Figs. 2 and 3) for the interaction of ferric chloride and potassium molybdicyanide. The composition of the complex would, therefore, be represented by the formula $KFe^{III}Mo^{IV}(CN)_8$, according to the reaction,

$$FeCl_3 + K_4Mo(CN)_8 \rightarrow KFe^{III}Mo^{IV}(CN)_8 + 3\,KCl.$$

The formation constant of the complex was determined by the method followed by Mukherji and Dey[10] for the reaction

$$mA + nB \rightleftharpoons AmBn,$$

where $m/n = 1$ or $m = 1$ or $m = n = 1$

The formation constant is

$$K = \frac{x}{(a - x)(b - x)},$$

where x is the concentration of the complex, and a and b are the initial concentration of ferric chloride and potassium molybdocyanide respectively. Taking two concentrations a_1 and a_2 and b_1 and b_2 of the reactants giving the same optical density. (that is the same value of x),

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

or

$$x = \frac{a_1b_1 - a_2b_2}{(a_1 + b_1) - (a_2 + b_2)}.$$

Knowing the value of x from the above equation, K is calculated from different values of a and b. Taking two concentrations of Fe^{3+} and $Mo(CN)_8^{4-}$ at the optical density 0·20 (Fig. 2), and the value of x from the above equation as $2{\cdot}19 \times 10^{-4}M$, the value of K was found to be $1{\cdot}37 \times 10^4$.

The free energy of formation of the complex was calculated with the help of the expression

$$\Delta F^\circ = -RT \ln k,$$

where ΔF° is the standard free energy change, R, the gas constant and T, the absolute temperature. The free energy of formation of ferric molybdocyanide complex works out to be −5·75 kcals. at 20°.

Potentiometric titrations carried out at different concentrations of potassium molybdicyanide with ferrous sulphate give the combining ratio of Fe^{2+} to $Mo(CN)_8^{3-}$

as 1:1, indicating the formation of the complex $KFe^{II}Mo^{V}(CN)_8$, according to the reaction,

$$FeSO_4 + K_3Mo(CN)_8 \rightarrow KFe^{II}Mo^{V}(CN)_8 + K_2SO_4.$$

This method, in addition to providing information regarding the composition of the iron^{II} molybdicyanide complex, has demonstrated the utility of a new electrode (the $Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ system at bright platinum) for investigating the reaction between heavy metal ions and potassium molybdo- and molybdicyanide. This electrode could be used successfully for studying the precipitation reaction between potassium molybdocyanide and Ni^{II}, Co^{II}, or Cu^{II}.

Zusammenfassung—Auf Zugabe von Eisen(III)-ionen zu einer Lösung von Kalium-Molybdocyanid bildet sich augenblicklich ein blauer, wasserlöslicher Komplex. Die Zusammensetzung des Komplexes wurde auf grund eines Job-Diagrammes und nach der Methode der Neigungsverhältnisse als folgende ermittelt: K Fe(III)Mo(IV)$(CN)_8$. Die Bildungskonstante beträgt $1{\cdot}37 \times 10^4$. Die freie Bildungsenergie wurde zu $-5{\cdot}57$ Cal bei 20°C berechnet. Ferrisulfat gibt auch mit Molybdicyanid einen blauen Komplex. Seine Zusammensetzung wurde durch Potentialmessungen an Gleichgewicht $Mo(CN)_8^{-4} \rightleftharpoons Mo(CN)_8^{-3} + e^-$ an einer blanken Platinelektrode ermittelt, und ist KFe(III)Mo(V) $(CN)_8$.

Résumé—Par addition de fer(III) à une solution de molybdo-cyanure de potassium, il se forme instantanément un complexe bleu soluble. La composition du complexe a été déterminée par la méthode des variations continues et par la méthode du rapport des pentes; ces méthodes montrent l'existence du complexe $KFe^{(III)}Mo^{(IV)}(CN)_8$. La constante de formation du complexe est $1{,}37 \cdot 10^4$ et l'énergie libre de formation calculée est $-5{,}57$ kcal. à 20°. Le sulfate de fer(II) donne aussi un complexe bleu avec le molybdo-cyanure de potassium. Sa composition a été étudiée par potentiométrie à une électrode de platine poli, utilisant le système oxydo-réducteur:

$$Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e$$

Les auteurs ont trouvé la formule suivante pour le complexe: $KFe^{(II)}Mo^{(V)}(CN)_8$.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—VII*

DETERMINATION OF COPPER AND IRON

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Summary—A simple complexometric determination of iron in the presence of copper has been devised. It is based upon the masking of copper with thiourea. Simultaneous reduction of iron is prevented by the addition of ammonium fluoride. The determination of iron is carried out in an indirect manner, *viz.* by back titration of an added excess of EDTA with lead nitrate using Xylenol Orange as indicator. The same procedure is employed in determining the sum of iron and copper, but without the previous masking of copper. The possibilities of determination of these two elements in the presence of others are discussed.

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IN view of the considerable difference between the stability constants of EDTA complexes with iron^{III} and copper^{II} (pK_{FeY} 25·1; pK_{CuY} 18·8) one could anticipate the possibility of direct consecutive determinations of the two elements. That this is actually possible has been demonstrated by potentiometric[1] as well as spectrophotometric[2] titrations of mixtures of iron and copper. In the field of visual titrations, however, no suitable procedure has so far been found. Such a method is possible only by the selective masking of copper. The masking agents hitherto used for copper in an acidic medium (thiosulphate, thiourea, thioglycollic acid), the action of which consists in reducing copper^{II} to copper^{I}, also react with iron^{III} ion, thus rendering this determination impossible. Preliminary experiments with the above mentioned substances have shown thiourea to be the most suitable reagent. Once copper has been masked by thiourea in a weakly acidic medium it no longer reacts with an added excess of EDTA—the solution remains colourless. The presence of iron gives rise to a brown coloration or even to a precipitate which, however, readily dissolves on the addition of EDTA; the solution is then yellow in colour because of the formation of an iron-EDTA complex. By back titration of an added excess of EDTA with lead nitrate using Xylenol Orange as indicator somewhat low results were obtained. At higher concentrations of iron, the indicator changes were blurred, which was probably caused by displacement of the iron^{II} present and by blocking of the indicator. This drawback can easily be eliminated by preventing the reaction of iron with thiourea by means of another complexing agent—in our case by the addition of ammonium fluoride. The colourless fluoride complex of iron^{III} is virtually inactive towards thiourea. The masking of copper by thiourea also has the advantage that a quite colourless copper^{I} complex is formed. The above method can be applied to the determination of iron even at high concentrations of copper.

EXPERIMENTAL

Reagents

0·05*M* solutions of $FeCl_3$, $CuSO_4$, $Pb(NO_3)_2$ and EDTA were prepared from reagent grade chemicals. Their concentrations were controlled by suitable complexometric methods. Other

* Part VI—Rudolf Přibil and Vladimír Veselý, *Talanta*, 1961, **8**, 565.

reagents were 20% thiourea, 1*M* ammonium fluoride and 0·5% Xylenol Orange solutions, and solid hexamethylenetetramine.

1. *Determination of iron in the presence of copper*

To the slightly acid solution add ammonium fluoride in excess. The blue-greenish coloration of the solution changes to pure blue. The solution of thiourea is then slowly added till discoloration of the solution occurs, plus 2 ml in excess, followed by the addition of an excess of EDTA solution. The mixture turns to yellow because of the formation of an iron-EDTA complex. The pH is adjusted to 5–5·5 with hexamethylenetetramine and the solution titrated with lead nitrate solution until the indicator changes from yellow to violet. The results of these titrations are listed in Table 1.

TABLE I—DETERMINATION OF IRON AND COPPER

(1 ml of 0·05*M* EDTA ≡ 2·7925 mg of Fe or 3·177 mg of Cu)

Taken, *mg*		Found, *mg*		Remarks
Fe	Cu	Fe	Cu	
2·83	32·40	2·84	32·28	
28·34	16·21	28·34	16·05	
2·83	16·21	2·82	16·30	
56·68	16·21	56·80	16·12	
2·83	162·10	2·95	162·24	During the titration a white precipitate appears but does not disturb the end-point.
14·18	64·84	14·26	64·62	
141·77	3·24	141·72	4·35	The end-point is less sharp (after screening of Cu) because of the slight blocking of Xylenol Orange 105 ml of EDTA used.
141·77	162·10	141· 68	162·41	

A closer investigation of the reaction of the FeF_6^{3-} complex with thiourea has revealed that microgram amounts of iron^{II} are formed (slightly positive reaction with phenanthroline). The concentration of the iron^{II} ions is so low, however, that it does not affect the results ($pK_{FeY} = 13·9$) and, what is very important, the colour change of the indicator. As one sees from Table I, quite reliable results are obtained in determining 3–100 mg of iron and 3–150 mg of copper in 150 ml of solution.

2. *Determination of copper in the presence of iron*

The literature describes several complexometric methods for this determination. All are based upon the masking of iron by means of ammonium fluoride in a very weakly acidic medium followed by direct titration of copper with EDTA using a suitable indicator. Theis[3] recommends Chromazurol S and pH 6–6·5. Wehber,[4] in titrations of copper using Variamine Blue B as indicator (pH 5·5), presents a case of masking 170 mg of iron by the addition of 1·2 g of ammonium fluoride. Lassner[5] also utilises ammonium fluoride in the determination of copper in the presence of iron and nickel.

In view of the fact that copper can be titrated directly with EDTA using Xylenol Orange as indicator and trace amounts of phenanthroline as "catalyst",[6] this method has also been tried in the presence of iron masked by ammonium fluoride. However, the experiments met with complete failure. This can be simply explained as caused by the fluoride complex, FeF_6^{3-}, being "sufficiently" dissociated to react with such a sensitive indicator as Xylenol Orange. Because of the blocking of the indicator the titration of copper cannot be carried out at all. Our experience is that the masking of iron with ammonium fluoride is never quite reliable. A much better method we consider to be the differential determination, *i.e.* one aliquot is used for the determination of iron according to the procedure described above, and another for the determination of the sum of the iron and copper

using the same method, except that no fluoride and thiourea are added. The results for copper are also given in Table I.

DISCUSSION

The described determination of iron and copper is very simple and affords reliable results over considerable concentration ranges of the two components (3–100 mg of iron and 3–150 mg of copper in 150 ml of solution). The applicability of a back titration with lead nitrate as titrant and Xylenol Orange as indicator, characterised by one of the most contrasting changes in colour at the end-point, can very easily be extended to analyses of mixtures containing more components. Thus an Fe-Al-Cu system can, in principle, be analysed in such a way that one aliquot is used to determine the sum of all the three elements, another to determine the sum of iron and copper after previous masking of aluminium with fluoride, and a third to determine iron after masking aluminium and copper with ammonium fluoride and thiourea respectively. Other combinations, encountered chiefly in analyses of special alloys, are the subject of further study and will be referred to elsewhere.

Zusammenfassung—Eine einfache Methode zur komplexometrischen Bestimmung von Eisen in Gegenwart von Kupfer wurde ausgearbeitet. Kupfer wird mit Thioharnstoff maskiert. Gleichzeitige Reduktion des Ferrieisens wird durch Zusatz von Ammoniumfluorid verhindert. Die Bestimmung des Eisens erfolgt indirekt durch Rücktitration eines Überschusses von ÄDTE mit Bleinitrat unter Verwednung von Xylenolorange als Indicator. Dieselbe Titration ohne Maskierungsmittel dient zur Bestimmung der Summe Fe + Cu. Weitere Möglichkeiten der Bestimmung beider Elemente nebeneinander werden diskutiert.

Rèsumè—Les auteurs ont mis au point un simple dosage complexométrique du fer en présence de cuivre. Le cuivre est complexé par de la thiourée. La réduction simultanée du fer est évitée par addition de fluorure d'ammonium. Le dosage du fer est réalisée indirectement, c'est-à-dire par titrage de l'excès d'EDTA par du nitrate de plomb avec le xylénol orange comme indicateur. Le même procédé est employé pour doser la somme Fe + Cu, mais sans avoir complexé préalablement le cuivre.

Les possibilités de dosage de ces deux éléments en présence d'autres sont discutées.

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SHORT COMMUNICATIONS

A method for the determination of dixanthogens

(*Received* 6 *March* 1961. *Accepted* 19 *June* 1961)

A METHOD for the determination of dixanthogens has been developed based on the action of chloramine-T on dixanthogen. The action of chloramine-T on xanthates has been studied by Rao and Murthy[1] who have utilised the reaction as a means of determining carbon disulphide after converting it into ethyl xanthate. It was suggested that the reaction can be extended to dixanthogens and so experiments were conducted to study the action of chloramine-T on diethyl, dibutyl and diamyl dixanthogens, with a view to standardising their methods of determination.

Reagents

Chloramine-T: 0·1*N* solution prepared by dissolving a recrystallised sample of chloramine-T (14·5 g per litre) and standardising iodimetrically in an acid medium as described earlier.[2,3]

Diethyl dixanthogen: Pure potassium ethyl xanthate was oxidised by iodine to obtain an insoluble oily diethyl dixanthogen. The oil was extracted with petroleum ether and the solvent evaporated in vacuum. The resulting diethyl dixanthogen had a melting point[4] of 28°. Analysis for sulphur (Carius) 53·12%; calculated 52·93%.

Dibutyl and diamyl dixanthogens were prepared under similar experimental conditions using the corresponding freshly prepared xanthates.

Dixanthogens are insoluble in water, but soluble in alcohol. Alcohol solutions of dixanthogens of known concentration were therefore used for purposes of oxidation. Alcohol is not oxidised by chloramine-T under the experimental conditions employed.

Procedure

A known amount of dixanthogen was mixed with an excess of acidified chloramine-T (10 ml of 0·1*N* with 5 ml of 2*N* HCl) in an Erlenmeyer flask and set aside for 1 hr. Then 10 ml of 10% potassium iodide were added and the liberated iodine was titrated against standard thiosulphate solution. From the amount of chloramine-T consumed the number of equivalents of the oxidant required per mole of dixanthogen was calculated. The experimental results were found to be reproducible and are presented in Table I.

TABLE I. OXIDATION OF DIXANTHOGENS BY CHLORAMINE-T

Dixanthogen	Dixanthogen taken, *moles* × 10^5	Chloramine-T consumed, *equivalents* × 10^4	Chloramine-T per mole of dixanthogen, *equivalents*
Diethyl	2·60	6·77	26·03
	1·92	5·00	25·93
Dibutyl	1·86	3·47	18·71
	2·02	3·80	18·84
Diamyl	1·78	3·19	17·86
	2·06	3·66	17·74

The above table shows that 1 mole of diethyl dixanthogen consumes 26 equivalents of

chloramine-T. This can be explained by the following mechanism, which is similar to that proposed for the oxidation of xanthate by chloramine-T in acid medium:[1]

$$C_2H_5O{-}\overset{\overset{S}{\|}}{C}{-}S{-}S{-}\overset{\overset{S}{\|}}{C}{-}OC_2H_5 + 13O + 7H_2O \rightarrow 2C_2H_5OH + 4H_2SO_4 + 2HCOOH$$

This quantitative reaction can be employed as an elegant method for the determination of diethyl dixanthogen. Reactions between dibutyl and diamyl dixanthogens and chloramine-T were found to be more complicated, consuming only 18–19 equivalents of chloramine-T instead of 26 equivalents. The heavier alkyl radical attached to the carbon atom is perhaps responsible for the incomplete oxidation of carbon disulphide (xanthate or dixanthogen) to formic acid and sulphuric acid. However, with calibration even these can be estimated conveniently.

Acknowledgement—The author wishes to express his grateful thanks to Prof. M. R. A. Rao for his keen interest in the work.

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Summary—One mole of diethyl dixanthogen reacts with 26 moles of chloramine-T, and this reaction can be used for the determination of the dixanthogen. Higher alkyl dixanthogens react in a more complicated fashion, but may still be estimated using an empirical correction.

Zusammenfassung—Ein Mole Diäthyldixangthogenat reagiert mit 26 Molen Chloramin-T, was zur Bestimmung von Dixanthogenat herangezogen werden kann. Höhere Alkylxanthogenate reagieren in komplizierter Weise, können jedoch gleichfalls bestimmt werden, wenn eine empirische Korrektur angebracht wird.

Résumé—Une mole de diéthyldixanthogène réagit sur 26 moles de chloramine T; cette réaction peut être utilisée pour le dosage du dixanthogène. Les alcoyl dixanthogènes supérieurs réagissent de manière plus compliquée, mais ils peuvent encore être dosés en faisant une correction empirique.

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A self-sampling indicator tube for carbon dioxide

(*Received* 8 *May* 1961. *Accepted* 20 *May* 1961)

FOLLOWING the development of an indicator tube for the determination of oxygen in air,[1,2] the production of a similar type of test for carbon dioxide covering the range 10–90% has been investigated. This work was undertaken mainly to provide a simple and rapid means of obtaining the correction for the oxygen tube when it is used in the presence of appreciable amounts of carbon dioxide,[1,2] produced by combustion or respiration. Such a test would also be useful in industrial applications where the oxygen content of an atmosphere has to be reduced to minimise fire or explosion risks (*e.g.* in the grinding of inflammable powders such as sulphur) by dilution with carbon dioxide or flue gases which contain a high proportion of carbon dioxide.

Both the oxygen and carbon dioxide tests employ reagents contained in evacuated glass tubes. To use the tubes, the sealed end is broken and the entering gas changes the colour of the reagent over a distance which depends on the concentration of reacting gas (oxygen or carbon dioxide).

Of the many fairly rapid methods available for determining carbon dioxide, most are of the titrimetric or colorimetric type and utilise the absorption of carbon dioxide by alkalies and the measurement of the original and residual volumes, or the reaction with an acid/alkali indicator.

Initially, attempts were made to use tubes in which silica gel and alumina were impregnated with phenolphthalein, bromothymol blue or alkali blue indicators. Although some of these showed a suitable colour change, the chemical reaction was not sufficiently rapid to produce a sharp front. However, when acid-washed sand was impregnated with rosaniline hydrochloride which had been decolorised with hydrazine hydrate,[3,4] carbon dioxide in concentrations of 5% and above rapidly restored the pink colour of the reagent and gave a sharp front sufficiently stable for its position to be marked. Powdered glass, alumina, and silica gel pretreated by heating to 1200°, were also tried but, in each case, rapid fading of the colour occurred.

The method of preparation of the tubes is as follows:

160 g of acid-washed sand, as near colourless as possible and between 50 and 100-mesh in size, are placed in a bottle fitted with a bung and a glass stopcock. Eight ml of a 1% rosaniline hydrochloride in methanol solution are added, and the contents are shaken until a uniform pink colour develops. The methanol is removed by vacuum drying at room temperature. After a further period of mixing, nitrogen is admitted to the bottle, and 0.12 ml of 99–100% hydrazine hydrate is added. The bottle is again shaken until the pink colour is completely discharged and a slightly damp, almost white mixture remains. At this stage, 0.4 g of magnesium carbonate (sieved through a 200-mesh sieve and dried at 110°) is added, and the bottle is purged with nitrogen and again shaken. The purpose of the magnesium carbonate is to produce a free-flowing mixture capable of being poured into tubes. The mixture is then placed in a hopper and subsequently allowed to pour into glass tubes, which are plugged with a disc of asbestos paper and a phosphor-bronze gauze plug, evacuated and sealed. The tubes are of about 5-mm bore and 25-cm length, 20 cm of which are filled with reagent.

Atmospheric oxygen should be prevented from reaching the mixture as far as possible, as this will oxidise part of the hydrazine, thus increasing the sensitivity of the tubes and making them unsuitable for the range of carbon dioxide contents required.

As with the oxygen tubes, to make a test the sealed end is broken in the atmosphere to be tested, and 5 sec later the position of the front is marked. The ratio (F) of length of pink colour to the total length of reagent is found and the carbon dioxide concentration (P) is obtained from a table calculated from the formula,

$$P = \frac{100aF}{1 - F + aF},$$

where a, the batch constant

$$= \frac{\text{Volume of carbon dioxide in ml absorbed per cm length}}{\text{Volume of residual gases in ml per cm length}}.$$

This formula is similar to that used for the oxygen tube and is derived in a similar manner.

A figure for the batch constant can be found by breaking a number of tubes of the same batch in an atmosphere of known carbon dioxide content and determining an average figure by calculation. Normally this calibration is done with 50% of carbon dioxide in air.

Experimental figures are similar to figures calculated from the formula over the range 10–90% of carbon dioxide. Below 10%, the front becomes diffuse and at about 5% no colour is visible at all because of rapid fading within the initial 5 sec. At ordinary temperatures and pressures, the test has been found to give results reproducible to within about 1 part in 20 of the carbon dioxide content of the sample under test. This degree of accuracy is ample for making the necessary correction to results obtained from the oxygen tubes.

The quantity of active material used is not important, neither are the dimensions of the retaining tube if the tube has a uniform bore. In principle, the tube will cover the range 0–100% of carbon dioxide. The quantity of reagent impregnated on the base can be altered over a very wide range, to give greater accuracy over different parts of the scale. For example, tubes have been made which are accurate to about 0.1% over the range 98–100% of carbon dioxide.

Little work has been done on the effect of other gases, as the order of concentration of any interfering gas would need to be the same as that of the carbon dioxide before any adverse effect would be possible.

As with the oxygen tubes based on silica gel, these tubes suffer from the disadvantage of requiring

batch calibration. Nevertheless, the test can be completed in 1 min, and the tubes appear to suffer no deterioration on keeping for at least 1 year.

The self-sampling indicator tube for carbon dioxide described in this paper is the subject of a provisional patent.[2]

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Summary—A simple indicator tube for the determination of carbon dioxide in an atmosphere is described. The test has been designed to cover the range 10–90% of carbon dioxide in the presence of oxygen and nitrogen or other inert gases. Estimations, accurate to about 1 part in 20, can be completed in 1 min. The prepared tubes are stable for at least 1 year.

Zusammenfassung—Die Herstellung einer einfachen Anzeigerohres zur Bestimmung von Kohlendioxyd in der Luft wird beschrieben. Das Gerät ist geeignet für Mengen von 10–90% Kohlendioxyd in Gegenwart von Sauerstoff, Stickstoff oder anderen inerten Gasen. Bestimmungen mit einer Genauigkeit von 1 Teil in 20 können innerhalb einer Minute ausgeführt werden. Die Beschickten Röhren könne für mindestens ein Jahr gelagert werden.

Résumé—Les auteurs décrivent un simple tube indicateur pour le dosage de l'anhydride carbonique. L'essai a été conçu pour couvrir le domaine 10–90 pour cent d'anhydride carbonique en présence d'oxygène et d'azote ou d'autre gaz inertes . Les dosages, précis à environ 1 pour 20, peuvent être réalisés en une minute. Les tubes préparés sont stables pendant au moins un an.

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Photocolorimetrische Zirkoniumbestimmung in Magnesium-Speziallegierungen mittels Morin

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EINLEITUNG

BEREITS in unserer früheren Arbeit[1] (und später auch die ungarischen Arbeiter A. Schneer und Mitarbeiter[2,3]) haben wir auf die Möglichkeit einer einfachen und schnellen photocolorimetrischen Zirkoniumbestimmung unter Ausnützung des gelben Zirkonium-Morinkomplexes hingewiesen. Nach Anwendung der Methode für die Zirkoniumbestimmung in Carbiden (in Isolaten, herstammend von der Isolierung von Strukturbestandteilen aus mit Zirkonium legierten Auftragmetallen) haben wir diese Methode für die Zirkoniumbestimmung in mit diesem Metall legierten Magnesium-Speziallegierungen ausgearbeitet. In Zusammenhang mit der eigentlichen Methode für die Zirkoniumbestimmung überprüften wir zugleich die Genauigkeit der Bestimmung von nicht in dem Grundmetall gelöstem Zirkonium durch Lösen der Probe in verdünnter Schwefelsäure und Chlorwasserstoffsäure.

ZIRKONIUMBESTIMMUNG MITTELS MORIN

Zirkonium liefert bei Gegenwart von Morin in Chlorwasserstoffsäure einen intensiv gelb gefärbten Komplex, welcher bei Anwesenheit von Alkohol sehr gut löslich ist. Die optimale Chlorwasserstoffsäurekonzentration beträgt ca. 0,5–0,6N,[1] die Morinkonzentration 0,02–0,01%, der Alkoholanteil

der Lösung 30%. Die Intensität der Ausfärbung ist schwach von der Zeit und der Temperatur abhängig, sodass empfohlen wird die Farbmessung stets nach einer genauen Zeit nach der Ausfärbung durchzuführen (20 oder 60 Minuten) und die Lösungen bei 20° zu halten. Die Abhängigkeiten sind im Einzelnen in der Arbeit[1] enthalten.

Die Reaktion von Zirkonium mit Morin ist weitgehend selektiv, sodass allgemein kein Trennungsverfahren angewendet werden braucht. Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, die Alkalimetalle stören nicht (vergleiche Tab. I.), Chloride, Perchlorate und Sulfate sind ohne Einfluss. Al stört nur in sehr grossen Mengen, ähnlich wie das Phosphat-Ion. Bei Anwesenheit von Fluoriden ist die Reaktion nicht durchführbar, man kann vielmehr durch Zusatz von Fluorid den Komplex entfärben. Eine bedeutend weniger intensive Gelbfärbung mit Morin gibt auch Ti, die Störung kann jedoch durch Anwendung einer Korrektionskurve eliminiert werden.

TAB. I. VERGLEICH DER MITTELS MORIN UND MITTELS PHENYLARSINSÄURE ERHALTENEN ERGEBNISSE DER ZIRKONIUMBESTIMMUNG

Probe	Zr zugesetzt, *mg*	Morin	Zr gefunden *mg*, mittels Phenylarsinsäure	Differenz beider Methoden
200 mg Mg	0	0	—	—
200 mg Mg 5 mg Ce	0	0	—	—
200 mg Mg 5 mg Zn	0	0	—	—
200 mg Mg	0,15	0,155	—	—
200 mg Mg	0,30	0,292	—	—
200 mg Mg	5,00	—	5,60	—
		in %	in %	in %
1	—	0,064 0,070	0,15	0,08
2	—	0,46 0,45	0,52	0,06
3	—	0,50 0,52	0,60	0,09
4	—	0,72 0,74	0,83	0,10

Lösungen

Morinlösung: 0,2g reinstes Morin werden in 100 ml Alkohol (Methyl—oder Äthylalkohol) gelöst.
HCl: 1:1 und 0,6N.
H_2SO_4: 5% ig.
Ascorbinsäurelösung: 2% in destilliertem Wasser.

Arbeitsgang

Da die Reaktion sehr empfindlich ist, wird eine grössere Einwage in einen Messkolben gebracht und von dieser Vorratslösung ein kleiner Teil zur eigentlichen Bestimmung verwendet. Durch dieses Verfahren wird gleichfalls der Einfluss einer Unhomogenität der Legierung beseitigt und die Lösung kann zu weiteren Bestimmungen gebraucht werden.

Je nach dem Zr-Gehalt werden 1–3g der Legierung in ein Becherglas eingewogen und mit 60 ml HCl 1:1 in Lösung gebracht. Nach Auflösen wird die Lösung in einen 250ml fassenden Messkolben filtriert, das Filter mit dem ungelösten Rückstand im Pt-Tiegel verascht, der Rest mit wenig Ammoniumpersulfat geschmolzen,[4] mit wenig 5% iger H_2SO_4 ausgelaugt und dem Haupteil im Messkolben zugegeben. Der Kolben wird nun mit 0,6N HCl bis zur Marke gefüllt.

Von dieser Vorratslösung werden 10 ml in einen 100 ml fassenden Messkolben pipetiert, 5 ml der Ascorbinsäurelösung zugesetzt und mit 0,6N HCl zur Marke gefüllt. Von dieser zweiten Lösung werden wieder 10 ml in ein kleines Becherglas gebracht, 5 ml Alkohol (Methyl—oder Äthylalkohol) zugegeben und mit 1 ml der Morinlösung versetzt. Die Lösung wird gemischt, das Becherglas in einen Thermostaten bei 20° gestellt und nach genau 20 oder 60 Minuten gemessen.

Die Messung wird vorteilhaft mit dem Hilger-Spekker-Absortiometer unter Benützung der Hg-Lampe und den Filtern OB 2 und Wratten 50 (Isolierung der Wellenlänge von 436 mμ) durchgeführt. Wasserwert 1,0, Schichtstärke 10 oder 5 mm. Der Zirkoniumgehalt kann direkt mit Hilfe einer Eichkurve abgelesen werden, wie es unsere Eichkurve auf Abb. 1 für eine Einwage von 2,5g in den 250 ml Messkolben zeigt.

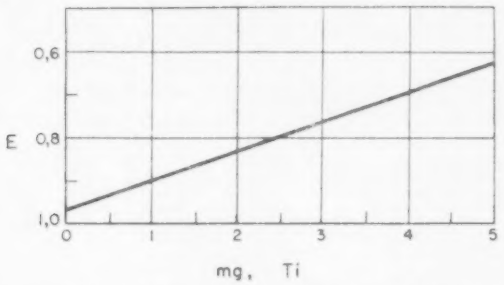

ABB. 1.—Eichkurve für die Zirkoniumbestimmung. 1—für Messungen nach 20 Minuten, 2—nach 60 Minuten für 10 mm Schichtdicke.

Die Eichkurve

Zur Herstellung der Eichkurve wurden 10 mg metallisches, spektralreines Zirkonium (Johnson & Matthey, London) im Platintiegel in 2 ml HNO_3 und einigen Tropfen HF gelöst und dann mit 2 ml H_2SO_4 abgeraucht. Da die Anwesenheit von F-Ionen die Reaktion stört, wurde das Abrauchen nach Anfeuchten mit einigen Tropfen Wasser wiederholt. Nach Auflösen der Sulfate in 5% iger H_2SO_4 wird die Lösung auf 100 ml aufgefüllt und so eine Lösung mit 0,1mg Zr/ml erhalten. Diese Lösung wird in Mengen von 0,5 1,0 . . . 5ml in einen 100 ml Messkolben pipetiert und nach Zusatz von Ascorbinsäurelösung wie beschrieben verfahren.

Die Korrektionskurve für Titan

Für die Konstruktion der Korrektionskurve für Titan wurde das gleiche Verfahren wie für das Zirkonium benützt, nur die Standartlösung wurde konzentrierter hergestellt, so dass 1 ml der Lösung 1 mg Ti enthielt.

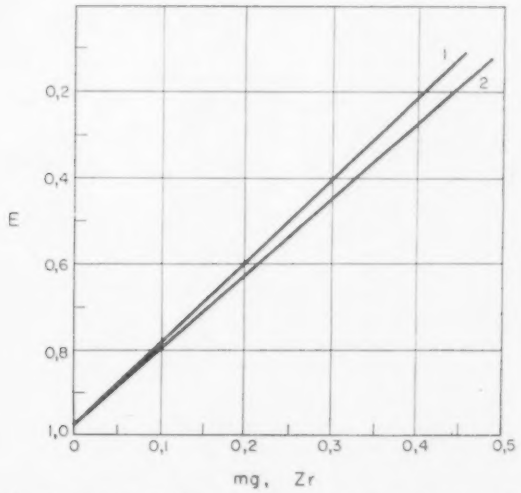

ABB. 2.—Korrektionskurven für die Zr-Bestimmung bei Titananwesenheit. 10 mm Schichtdicke.

Wie aus Abb. 2 zu sehen ist, verläuft die Korrektionskurve für Ti selbst bei 10 mal grösserer Konzentration bedeutend flacher—die Reaktion für Zr ist ca. 25 mal empfindlicher. Im Durchschnitt kann geschlossen werden, dass bei 10 mal grösserem Gehalt an Ti als an Zr die Bestimmung mit hinreichender Genauigkeit ohne vorangehende Abtrennung des Ti durchgeführt werden kann.

Die nach der angeführten Methode erhaltenen Ergebnisse wurden mit direkter gravimetrischer Bestimmung von Zr mittels Phenylarsinsäure kontrolliert[1]; einige Ergebnisse führt Tab. I. an. Wie zu sehen, ist bei der colorimetrischen Bestimmung das Grundmetall Mg selbst in grössten Mengen ohne Einfluss. Die mittels Phenylarsinsäure erhaltenen Werte sind in allen Fällen, selbst bei der Standartlösung höher, als der Tatsache entspricht. Gleichzeitig werden in dieser Tabelle zahlenmässige Ergebnisse an Betriebsproben angeführt.

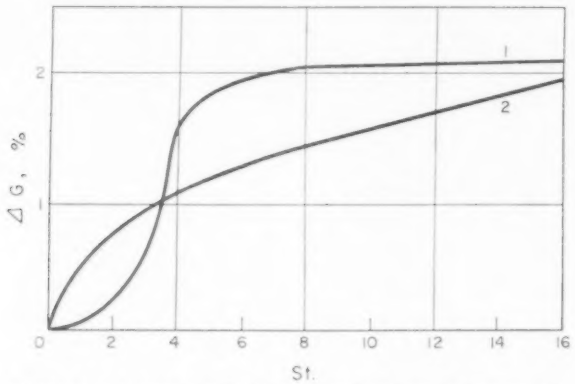

Abb. 3.—Löslichkeit in % von metallischem pulverförmigem Zirkonium (Degussa) bei 20°
1—in 10% HCl, 2—in 10% H_2SO_4.

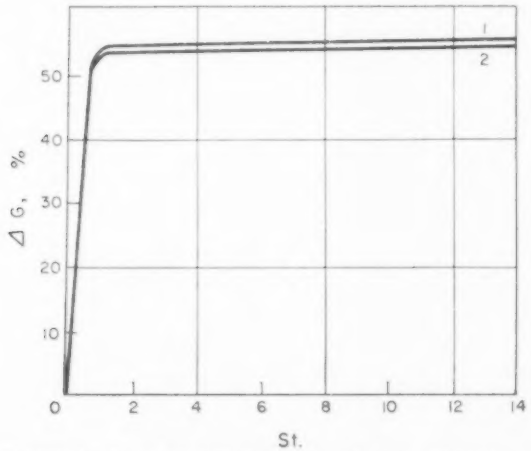

Abb. 4.—Löslichkeit in % von metallischem pulverförmigem Zirkonium (Degussa) bei 90°.
1—in 10 % HCl, 2—in 10% H_2SO_4.

UNTERSUCHUNG DER LÖSLICHKEIT VON METALLISCHEM ZIRKONIUM IN CHLORWASSERSTOFF UND SCHWEFELSÄURE

Die schlechte Löslichkeit von metallischem Zirkonium in Säuren führt zu der Annahme, dass das in der Legierung anwesende metallische Zirkonium beim Lösen der Probe in Chlorwasserstoffsäure als unlöslicher Schlamm zurückbleibt, während das in metallische Phasen eingegangene Zirkonium in Lösung geht.* Informative Zirkoniumbestimmungen nach Auflösen der Probe Nr. 3 in HCl 1:2 und 2:1 ohne nachträgliches Erwärmen und nach Abfiltrieren des ungelösten Rüskstands zeigten jedoch steigende Resultate: 0,27% und 0,42% Zr. Nachträglich durchgeführte Beständigkeitsprüfungen von Zirkonium-Metallpulver (Degussa) in HCl- und H_2SO_4—Lösungen bei 20 und 90°C zeigten, dass bereits zu Beginn der Säureeinwirking und niedriger Temperatur grosse Anteile an

* So wird z.B. nach dem britischen Standart B.S.2970:1959, Appendix A gearbeitet: Das "wirksame" Zirkonium ("available zirconium") wird durch Lösen der Probe in 30 ml HCl 1:2 auf lg und 5 Minuten Sieden bestimmt; das unter diesen Bedingungen nichtgelöste Zirkonium wird abfiltriert.

Zirkonium in Lösung gehen (Abb. 3 und 4), wobei die Löslichkeit mit der Temperatur stark ansteigt. Die erhaltenen Ergebnisse schliessen also eine Trennung des gelösten und ungelösten Zirkoniums mittels einfacher Säureauflösung der Probe aus.

Zusammenfassung—Zur Schnellbestimmung von Zirkonium in Legierungen wurde eine kolorimetrische Methode herangezogen die auf einer Farbreaktion mit Morin beruht. Die benötigte Zeit ist etwa eine Stunde, doch reduziert sich diese Zeit im Serienbetrieb. Grosse Mengen von Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, Cl^-, ClO_4^- und SO_4^{2-} stören nicht. Für Titan muss eine Korrektionskurve konstruiert werden. Fluorid stört.

Eine nähere Untersuchung zeigte, dass lösliches und unlösliches Zirkonium in Magnesiumlegierungen nicht einfach durch Lösen in Salz—oder Schwefelsäure getrennt werden können. Fein verteiltes Zirkoniummetall wird durch die beiden Säuren in beträchtlichem Ausmasse gelöst.

Summary—For the rapid determination of zirconium in magnesium alloys a colorimetric method based on colour formation between zirconium salts and morin can be used. The time needed for a simple determination is about 1 hr, but this can be reduced in routine analysis.

The reaction between zirconium and morin is not affected by large quantities of Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, chloride, perchlorate or sulphate. For Ti a correction curve can be constructed. Fluoride interferes with the colour development.

Investigation of the reactivity of zirconium metal and actual experience indicate that the soluble and the insoluble zirconium in magnesium-alloys cannot be separated by simple dissolution of the base metal in HCl or H_2SO_4. Finely divided zirconium is dissolved to a considerable extent by these acids.

Résumé—Pour le dosage rapide du zirconium dans les alliages de magnésium, on peut utiliser une méthode colorimétrique basée sur la formation d'une coloration entre les sels de zirconium at le morin. Le temps nécessaire pour un simple dosage est environ une heure, mais il peut être réduit dans une analyse de routine.

La réaction entre le zirconium et la morin n'est pas modifiée par de grandes quantites de Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, chlorure, perchlorate ou sulfate. Pour Ti, une courbe corrective peut être établie Le fluorure perturbe le développement de la couleur.

L'etude de la réactivité du métal zirconium et l'expérience présente indiquent que le zirconium soluble et le zirconium insoluble dans les alliages de magnésium ne peuvent pas être séparés par simple dissolution du métal dans HCl ou H_2SO_4. Le zirconium finement divisé est dissous à un degré considerable par ces acides.

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VLADIMÍR KABICKÝ

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Spectrophotometric determination of bismuth with Xylenol Orange after dithizone-chloroform extraction

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METHODS for the spectrophotometric determination of bismuth with Xylenol Orange have been described independently by the present authors[1] and by Cheng.[2] In general the two sets of results agree reasonably well.* In order to extend the applicability of the Xylenol Orange method, it was

* The present authors made a mistake in the calculation of the formation constant for the bismuth-Xylenol Orange complex. The correct value is $3{\cdot}3 \times 10^5$ in 0·1N nitric acid.

thought worthwhile to investigate a selective separation method for bismuth. Metals that interfere with the determination of bismuth rather seriously are copper, indium, titanium, zirconium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and iron.[1] Because as much as 10 mg of lead and 1 mg of thallium[1] do not interfere with the determination of bismuth,[1] the separation of bismuth from these two elements is not very important. When bismuth is to be determined in the presence of large amounts of lead, cupferron extraction[3] or oxychloride precipitation[4] is probably suitable. It is considered that the separation of bismuth by dithizone-chloroform extraction has a general applicability. However, there is some difference of opinion in the literature concerning the completeness of extraction of bismuth dithizonate.[5] From these considerations, extraction with dithizone has been studied in some detail, and the results are reported in the present paper.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Hitachi Model EPU-2A spectrophotometer, using 1-cm cells. A glass-electrode pH meter (Horiba Model M-3) was used for pH measurements. A shaking machine with a time switch was used for extractions.

Reagents

All the reagents used were of reagent grade.

Potassium cyanide: 35 g in 100 ml of water.

Ammonium citrate: 20 g of $(NH_4)_2HC_6H_5O_7$ in 100 ml of water.

Hydroxylamine sulphate: 30 g in 100 ml of water.

Dithizone: 0·10 g in 1000 ml of redistilled chloroform.

L-Ascorbic acid: 10 g in 100 ml of water.

Sodium fluoride: 0·10 g in 100 ml of water.

Xylenol Orange: 0·10 g in 100 ml of water.

Standard bismuth solution: Dissolve 0·500 g of bismuth metal in nitric acid and evaporate to dryness on a water bath. Dissolve the residue in 1:9 nitric acid and make up to 500 ml with the same solvent. From this stock solution (1·00 mg of bismuth per ml), prepare a working standard of appropriate concentration by dilution.

Procedure

Separation of bismuth. Transfer the sample solution (dilute nitric acid solution containing 10 to 100 μg of bismuth in a volume of 10 to 30 ml) to a separatory funnel. Add 7·5 ml of ammonium citrate solution and 5 ml of potassium cyanide solution. Adjust the pH of the solution to 9·4–10·2 with 1:1 ammonium hydroxide and dilute to about 50 ml with water. Shake the solution for at least 1 min with 10 ml of dithizone solution. When the layers have separated, drain off the chloroform phase into another separatory funnel. Extract with two further 10-ml portions of dithizone solution. Combine the extracts and discard the aqueous phase. Wash the extracts with 5 ml of 1:99 ammonium hydroxide.

Shake the organic phase for at least 1 min with 10 ml of 0·5*N* nitric acid. Repeat the back-extraction with another 10-ml portion of nitric acid. Discard the organic phase and collect the aqueous phase into a 100-ml porcelain dish. Evaporate the solution to dryness on a water bath.

Determination of bismuth. Dissolve the residue in 2·0 ml of 1·2*N* nitric acid and transfer the solution to a 25-ml volumetric flask. Wash the dish with small amounts (totalling not more than 15 ml) of water.

Add 1·0 ml of ascorbic acid solution, 1·0 ml of sodium fluoride solution, and 1·0 ml of Xylenol Orange solution, in the order mentioned. Dilute to the mark with water, mix, and measure the absorbance of the solution in a 1-cm cell at 530 mμ using water as the reference.

Construct a calibration curve by taking 0 to 100 μg of bismuth, adding ascorbic acid, sodium fluoride, and Xylenol Orange, and proceeding as described above.

Run a blank through the entire procedure.

RESULTS AND DISCUSSION

Determination of bismuth

In the method described by Cheng,[2] the absorbance of the bismuth-Xylenol Orange complex in 0·1N sulphuric acid is measured at 545 mμ. It appears that the absorption maximum varies with the

ratio of bismuth to Xylenol Orange.[6] Kotrlý and Vřeštál[6] titrated microgram amounts of bismuth in nitric acid photometrically at 530 mμ with EDTA. The molar absorptivity of 24,000 given by Cheng[2] is a little higher than the value of 16,000 obtained by the present authors.[1] The difference is probably caused by the purity of the Xylenol Orange reagents. Although Cheng[2] states that perchloric acid inhibits the formation of the bismuth-Xylenol Orange complex, the present authors[1] have not been able to observe this phenomenon.

Separation of bismuth

For the extraction of bismuth with dithizone-chloroform solution, Haddock[7] used a 0·1 % dithizone solution, while Hubbard[8] used a 0·006 % (w/v) dithizone solution. In the present work, a 0·01 % (w/v) dithizone solution has been used. The amounts of potassium cyanide (1·75 g) and of ammonium citrate (1·5 g) used in the present work are close to those used by Haddock.[7]

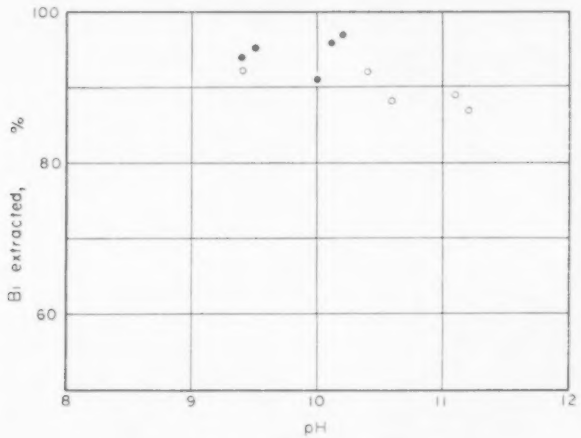

FIG. 1—Extraction of bismuth
○ In the presence of potassium cyanide
● In the presence of ammonium citrate and potassium cyanide

Recoveries of bismuth dithizonate from solutions containing potassium cyanide or ammonium citrate plus potassium cyanide are shown in Fig. 1. Forty or fifty μg of bismuth were taken in each case. The organic extract was evaporated to dryness. Two ml of 30 % hydrogen peroxide and 1 ml of concentrated sulphuric acid were added to the residue, and the solution was evaporated to dryness on a hot plate. The residue was treated with 2·0 ml of 1·2*N* nitric acid and the colour development was then carried out. At pH 9·4 to 10·4, 92 % (average) of bismuth is extracted from a solution containing potassium cyanide. In the presence of ammonium citrate and potassium cyanide, the pH of the solution does not change greatly upon the addition of ammonium hydroxide. At pH 9·4 to 10·2, the average recovery of bismuth is 94 %.

The effect on the overall recovery of bismuth of varying the nitric acid concentration used in the back-extraction is shown in Fig. 2. The experiments were carried out by the proposed procedure, using 50 μg of bismuth each time. By using 0·5 to 1·0*N* nitric acid, more than 95 % of the bismuth is recovered. With higher concentrations of nitric acid (>1*N*), oxidation of dithizone occurs markedly.

Table I summarises the results obtained in applying the proposed method in the presence of other metals. Most of the metals used were in the form of nitrate or sulphate. In the presence of aluminium (aluminium metal was dissolved in sodium hydroxide and the solution was then acidified with nitric acid) and zirconium (zirconium metal was dissolved in sulphuric acid in the presence of ammonium sulphate), the extraction of bismuth with dithizone is slow, and it is necessary to extract for as long as 15 and 5 min, respectively. The proposed method has been applied successfully to aluminium metal containing 40 to 150 ppm of bismuth.

Since indium is also extracted with dithizone in chloroform and more than 0·1 mg of this element interferes with the determination of bismuth,[1] ethyl ether extraction of indium bromide has been

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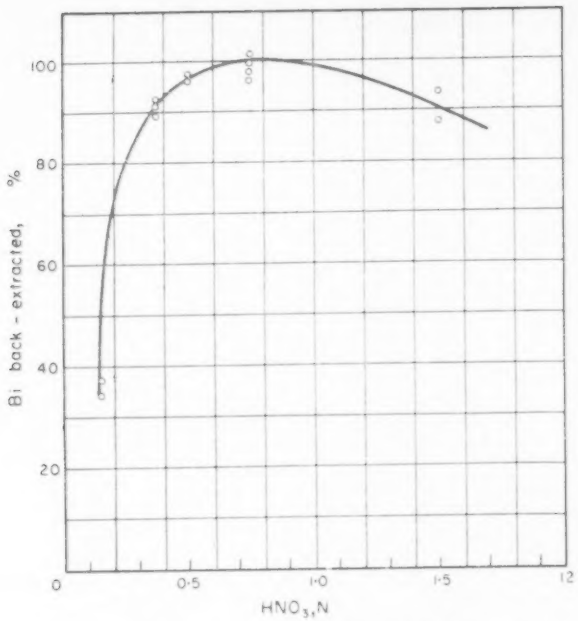

FIG. 2—Back-extraction of bismuth with nitric acid

TABLE I—DETERMINATION OF BISMUTH WITH XYLENOL ORANGE AFTER DITHIZONE-CHLOROFORM EXTRACTION

Addition, *mg*	Bi taken, *μg*	Bi found, *μg*[a]	Average recovery, %
—	20·0	19[b], 19[b], 18[c], 18[c]	93
—	100	101[b], 100[b], 97·6[c], 98·8[c]	99·3
Al 500	50·0	47·0, 46·5	93·5
Cr^{III} 20	50·0	47·0, 46·5	93·5
Cu 500	50·0	50·0, 50·0, 49·0, 48·0	98·5
Fe^{III} 100	50·0	49·6, 49·6	99·2
Mo^{VI} 55	50·0	49·5, 50·5	100
Nb 10	50·0	47·5, 46·5	94·0
Th 50	50·0	47·5, 49·5	97·0
Ti^{IV} 10	50·0	49·5, 47·5	97·0
Ti^{IV} 20	50·0	44·0, 44·0	88·0
U^{VI} 500	50·0	50·0, 50·0, 51·5, 51·5	102
V^{V}25	50·0	50·0, 48·5	98·5
W^{VI} 25	50·0	47·5, 48·0	95·5
Zr 25	50·0	48·0, 48·0	96·0
Zr 50	50·0	46·0, 46·0	92·0

[a] Correction applied for blank: 0·0 *μg* with no addition, Cu, and Fe; 0·2 *μg* with Th, V, W, and Zr 0·5 *μg*; with Mo; 1·2 *μg* with Cr, Nb, and Ti; and 4·7 *μg* with U.
[b] Time of shaking for each extraction: 1 min.
[c] Time of shaking for each extraction: 5 min.

studied (Table II). The procedure used was as follows: Twenty ml of sample solution, which is approximately 4·5*N* in hydrobromic acid, are shaken with three 10-ml portions of ethyl ether. The

aqueous phase is then transferred to a 100-ml dish and evaporated to dryness. (The organic phase that contains indium is discarded.) The residue is dissolved in 2·0 ml of 1·2*N* nitric acid, and the bismuth is determined according to the proposed method. The results are slightly low.

TABLE II—DETERMINATION OF BISMUTH AFTER REMOVAL OF INDIUM
(50·0 μg of bismuth taken in each determination)

Addition, *mg*	Bi found, μg[a]	Average recovery, %
In 10	44·1, 44·5	88·6
In 5·0	45·2, 46·1	91·3

[a] Correction applied for the blank (0·4 μg of Bi with 5 mg of In).

Summary—For the purpose of extending the applicability of the spectrophotometric determination of bismuth with Xylenol Orange, the separation of this element from interfering elements has been studied. Bismuth is extracted as its dithizonate with chloroform from an alkaline solution containing citrate and cyanide, then back-extracted into 0·5*N* nitric acid. After evaporation of the solution, the bismuth is determined spectrophotometrically with Xylenol Orange.

Zusammenfassung—Zwecks Ausdehnung des Anwendungsbereiches der spektralphotometrischen Bestimmung von Wismut mit Xylenolorange wurde die Abtrennung dieses Metalles von störenden Elementen studiert. Wismut wird als Dithizonat in alkalischem Medium in Gegenwart von Zitrat und Cyanid in Chloroform extrahiert und sodann in 0·5 N Salpetersäure rückgeschüttelt. Nach Abdampfen der Lösung wird Wismut mit Xylenolorange bestimmt.

Résumé—Afin d'étendre l'application de la méthode spectrophotométrique de dosage du bismuth par le xylénol orange, les auteurs ont étudié la séparation de cet élément des éléments gênants. Le bismuth est extrait à l'état de dithizonate par du chloroforme à partir d'une solution alcaline contenant du citrate et du cyanure, puis extrait à nouveau dans de l'acide nitrique 0,5 N. Après évaporation de la solution, le bismuth est dosé par spectrophotométrie avec le xylénol orange.

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BOOK REVIEWS

Advances in Analytical Chemistry and Instrumentation, Volume 1. Edited by CHARLES N. REILLEY. Interscience Publishers, Inc., New York, 1960. pp. vii + 445. $12.00.

IN the first volume of a proposed annual series the editor and contributors have achieved their goal in presenting chapters which "deal not only with significant new developments in idea and techniques, but also with critical evaluations and the present status of important, but more classical, methods and approaches". A well qualified group of workers was selected to prepare this volume.

Tetraphenylboron (TPB) as an Analytical Reagent. H. FLASCHKA and A. J. BARNARD, JR. (117 pages). This chapter provides a full treatment of the precipitation of potassium TPB as well as application to other metal ions and organic compounds. These authors also have provided detailed working directions for several of the procedures.

Recent Advances in Gas Chromatography Detectors. ROBERT B. SELIGMAN and FORREST L. GAGER, JR. (32 pages). Emphasis is placed on the development of the high sensitivity ionisation detectors; however, recent developments in flame detectors, and improvements in the density balance and thermal conductivity cells are included.

Trends in the Determination of Fluorine. C. A. HORTON. (47 pages). Discussion is limited primarily to developments since 1953. Especially valuable are the sections on difficulties and shortcomings of the past and present methods and the challenges for future investigations. No attempt was made to cover the determination of fluorine in organic compounds.

New Ideas in Organic Microanalysis Part I. C–H, O, N. Halogens, S, and Other Elements. WOLFGANG SCHÖNIGER. (42 pages). Information on modifications of classical methods is presented and reviewed critically. New methods, many of which were developed and tested in the author's laboratory, are included.

Theory of Electrode Processes. W. H. REINMUTH. (52 pages). The author surveys the rapidly growing volume of literature on the theoretical aspects of electrode reactions, and emphasises those publications of greater value and interest to analytical chemists.

The Analytical Chemistry of Thioacetamide. ERNEST H. SWIFT and FRED. C. ANSON. (53 pages). From the laboratories of the authors have come many of the more basic studies of the use of thioacetamide for the precipitation of metal sulphides. The authors review the literature thoroughly and point out the dangers of the indiscriminate use of thioacetamide as a substitute for hydrogen sulphide without more extensive investigations. Future trends in research in the field are discussed.

Near-Infrared Spectrophotometry. ROBERT F. GODDU. (78 pages). The development of commercially available spectrophotometers has produced a rapid increase in analytical research in the near-infrared region of 1 to 3 microns. The author makes excellent evaluations of recent work and predicts that the near-infrared region will continue to find greatest value in quantitative organic functional group analysis.

This volume of *Advances* will make a valuable addition to the libraries of many analytical chemists and analysts. Some chemists with more specialised interests might prefer to have such volumes divided and published as monographs or collections of more closely related topics. The additional cost of publication, however, probably is justified to provide the broad scope for those who wish to keep abreast of all developments in analytical chemistry. The editor and authors should be commended for the excellence of this volume, especially for the critical evaluations included in the presentations.

WILLIAM F. WAGNER

Gas Chromatography. Edited by HENRY J. NOEBELS, R. F. WALL and NATHANIAL BRENNER. Academic Press Inc., New York and London, 1961. pp. xvi + 463. 114s. 6d.

THIS volume comprises the thirty-four papers read at the Second Symposium on Gas Chromatography held under the auspices of the Analysis Instrumentation Division of the Instrument Society of America in June 1959. It reflects the present state of gas chromatography, which, despite its tender

years and the large flux of papers to which it still gives rise, is passing now into the stage of instrumentation and elaboration. The initial period of hectic development of detectors and columns, in face of the fundamental advancement of the technique, seems now to be passing into a period of consolidation and application which are the criteria of a mature technique. For example, in this volume there are papers concerned with process control systems embodying gas chromatography analysers, with general problems of design of gas chromatographic apparatus, with automatic fraction collection and with integration of peak areas. In this connection, it is ironical to note a wistful reference by A. T. James, in an amusing historical account of the birth of the technique, to the subject's "sealing wax and string" origins in A. J. P. Martin's laboratory. Just as is true of another subject which had its origins in a laboratory noted for its skill in handling "sealing wax and string," namely that of Rutherford, gas chromatography has very little to do nowadays with these primitive materials, as a glance through the volume under review will very quickly show. Indeed, part of the great power of the technique lies in the fact that it lends itself so naturally to instrumentation. In some circles, instrumentation is regarded as a euphemism for gadgeteering; it is not, though doubtless there are occasions when it may be so. Perhaps one of the dangers currently besetting gas chromatography is that its instrumentation could degenerate into elaborate contrivances which are not an integral part of the technique. One becomes aware sometimes of this possibility when reading through this collection of papers, but not often. A substantial portion of the book is concerned with detailed reports of separations, which, despite their specificity, are usually of general value because they are concerned with classes of compounds which are continually involved in analytical problems of current interest. The fundamental aspect of the technique, while not figuring so prominently as in earlier proceedings of this kind, is certainly not neglected and there are valuable reports of advances in fraction detection and column operation. Concluding the book is a bibliography of 1515 references to papers concerned with gas chromatography published in the period 1958 to June 1960, requiring 81 pages for its presentation. This bibliography is a continuation of the bibliography started in the volume in which were reported the proceedings of the First Gas Chromatographic Symposium held in 1957. The usefulness of this collection of titles, listed in alphabetical order of the authors, is limited greatly by the absence of a subject index to its contents.

The standard of presentation is up to the high quality associated with the publishers. The price, too, is well up to the level expected for this type of publication, but which few scientists have become accustomed to accept without complaint. Bearing in mind the high cost of the book, there is frequently an excessive expansiveness and leisureliness in the presentation of information which is irritating. Far too many chromatograms are given, and the practice of introducing numerous photographs of apparatus which convey little or nothing about the design and function of the apparatus is particularly to be deplored.

DESMOND BRENNAN

Spectrochemical Analysis. L. H. AHRENS and S. R. TAYLOR. Pergamon Press, London–Paris, 2nd Edition, 1961. 454 pp. £5. 5s.

THE scope of this excellently produced volume is more correctly described by the subtitle, "A treatise on the d.c. arc analysis of geological and related materials." It is the second edition of AHRENS' *Spectrochemical Analysis* (1950), but also incorporates much of AHRENS' *Quantitative Spectrochemical Analysis of Silicates* (1954). This edition has been revised up to December 1959, and, as an indication of the completeness of this revision, the bibliography has been extended from twenty-one pages to forty-six by the inclusion of references to articles published during the last ten years.

The book follows the same pattern as the first edition in being divided into two parts—"General Principles" and "The Elements." Chapters in the first part include an adequate summary of the origin of spectra, and discussions on physical features of the d.c. arc discharge, sample preparation and operating procedures, qualitative and quantitative analysis, enrichment procedures, and photographic photometry. Two excellent chapters on selective volatilisation and the effect of change of matrix on line intensity are included. The second part deals with general methods of analysis and with schemes for the analysis of silicates. Thereafter, methods are described for the determination of elements individually or in groups. The final chapter is concerned with the determination of major constituents. Wavelength tables are given in an appendix of seventy-one pages. Although the reviewer feels that

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the inclusion of such tables is not justified, it would be an advantage if the meaning of such notations as (aa), (bb), (M and S) and (S and W) were included at the beginning of the tables and not on pages 69 and 70.

The presentation of the book in two parts results in duplication in many instances, examples of which are the concentration procedure of Mitchell and Scott (pp. 130, 191–192), Jaycox's method (pp. 182, 299–300), volatilisation effects (pp. 81–87, 95, 123–124) and self-absorption (pp. 32–36, 99–101, 106–109). The reviewer regrets the author's decision to alter, as compared with the first edition, the method of presentation of the working curve (section 11–4), by using the abscissa for the intensity ratio. This is the more regrettable since numerous figures remain with the concentration on the abscissa (pp. 121, 122, 158, 159, 220, 239, 266). Although errors in a book of this size are inevitable, only two have been noted—the reference to Strock (1948b) on p. 61 should be 1948, and on p. 270, line 7, 11 mm should read 2.75 mm.

Direct photometric methods are mentioned in the introduction only, and a short discussion of such methods might have been included in the text, since they are now being employed both in industry and research for the analysis of non-conducting materials.

The above remarks in no way detract from the value of the book. It is an excellent publication and should be of great interest and use both to geochemists and to spectrochemical analysts dealing with either non-conducting powders or metallic samples.

R. O. Scott

Treatise on Analytical Chemistry. A Comprehensive Account in Three Parts. Part I, Theory and Practice, Volume 2. I. M. Kolthoff and Philip J. Elving, with the assistance of Ernest B. Sandell. Interscience Publishers, New York, 1961. pp. xx + 498. $16.00 (single), $14.00 (subscription).

This second volume of Part I of Kolthoff and Elving's Treatise follows the conceptual and organisational patterns established in Volume 1, with which most analytical chemists are now familiar. Volume 2 contains the concluding two chapters of Section B, on application of chemical principles to analytical chemistry, and nine of the chapters of Section C, on separations.

The first two chapters, by Leo Schubert and Irving May, deal with organic and inorganic applications of reactive groups as reagents. These chapters are primarily concerned with classifying types of reactions and reagents of analytical significance; the brief individual discussions of about thirty chelating agents will be found useful by many.

The editors have secured the services of L. B. Rogers to act as advisor for Section C, Separations, and Rogers has also contributed the opening chapter of this section, an excellent presentation of the common theory of separations. This is followed by a rigorous, rather general discussion of the phase rule (L.O. Case), two practical chapters on decomposition and dissolution of samples—inorganic (H. H. Willard and C. L. Rulfs) and organic (E. C. Dunlop), and chapters on separations by mechanical methods (H. C. Mattrow and E. D. Leipziger), diffusion methods, with emphasis on thermal diffusion (A. L. Jones and G. R. Brown), electromigration and electrophoresis (J. R. Cann), distillation (A. Rose), and vacuum methods (W. S. Horton).

No index has been provided; however, the editors state that Volume 3 will contain an index for Volumes 1, 2 and 3, and that subsequent volumes will be provided with individual indexes.

As was the case with Volume 1, the depth of treatment is sufficient in most cases to permit this volume to stand alone as a survey of, or introduction to, the topics covered. The lists of references at the ends of the chapters are more extensive than in the previous volume, and appear to cover the literature through 1958.

It is unfortunate that a tendency exists to compare Volume 2 with Volume 1, for Volume 2 suffers from such a comparison. Where the first volume showed a remarkable degree of unity, the second is more in the nature of a series of monographs. The first volume was nearly free from typographical and other flaws in production; the second has its full share. Minor, but rather jarring, defects in style have found their way into Volume 2, *i.e.*, "in two general ways may the McLeod gage be used". Such editorial lapses do not, of course, detract from the significance of this volume, but they do make it somewhat less readable, and therefore less desirable, than its predecessor.

David H. Klein

Oszillographische Polarographie mit Wechselstrom. J. HEYROVSKÝ und R. KALVODA, Akademie-Verlag, Berlin, 1960. pp. viii + 198. DM.23.

THIS book, in the German language, gives a survey of the technique of oscillographic polarography using alternating current. In it is collected most of the important published information on the subject, which is mainly from the numerous papers by Heyrovský and his co-workers. Theory and basic principles are given and the various methods of working, both direct and derivative, are described in detail. The influence of parameters such as temperature, frequency and cell and electrode capacity are considered and the effect of the degree of reversibility of the system being studied upon the resulting oscillogram, and kinetic phenomena in general, are discussed.

The electronic instrumentation associated with the method is described and some circuit diagrams are given, together with details of the commercially-available instruments. These are known as "Polaroscopes". In spite of the comparative simplicity of the instrumentation fuller descriptions would have been valuable in view of the novelty of the method.

The type of working which has proved most fruitful is a derivative system by which $\frac{dE}{dt}$ is plotted against the applied potential, E. This gives rise to an elliptical trace on the cathode-ray tube screen, upon which the changes in the voltage-time curve at constant current, caused by oxidation or reduction of a depolariser, appear as superimposed "cuts-in". The dynamic nature of the trace and the shape of the "cuts-in" make accurate quantitative measurement difficult. This type of polarography is therefore more satisfactory for qualitative studies, although semi-quantitative, or quantitative determinations are sometimes possible and useful. Considerable space is devoted to descriptions of methods for improving the quantitative measurement of the depths of these "cuts-in", including instrumental devices, such as the use of a double-beam cathode-ray tube with a calibrated Y shift on the reference beam and oscillographic and comparative titrations.

Important chapters describe the oscillopolarographic behaviour of many inorganic and organic species and special groups of substances such as noxious gases and vapours. These have great value because the most important application lies in the rapid qualitative, and sometimes semi-quantitative, characterisation of species, the oscillopolarographic behaviour of which is often very different from that observed by classical polarography. This has special value in organic polarography, since many compounds may be characterised, although they do not yield a conventional polarographic step.

Finally the book gives brief details of newer instrumental devices designed to replace the dynamic trace on the screen by a standing wave, by methods such as the use of a synchronised dropping mercury electrode. This should put the technique on a firmer quantitative basis. A bibliography of 172 references is appended.

The development of the oscillopolarographic techniques has been carried out almost entirely by Heyrovský and his co-workers in Prague, but apart from a small volume by Heyrovský and Forejt in 1953, this is the first book on the subject. It must, therefore, be welcomed as an important addition to the literature of polarography. It will assist the more general understanding of this technique, but it should be criticised for making these methods appear more important and universally applicable than they are at present. It is well written and adequately illustrated and a good balance is maintained between the various topics discussed. An English translation would be valuable.

G. F. REYNOLDS

Organic Analysis, Vol. IV. Edited by JOHN MITCHELL, Jr., I. M. KOLTHOFF, E. S. PROSKAUER and A. WEISSBERGER. Interscience Publishers, Inc., New York. 429 pp. $13.50.

THE titles and authors of the contributions to the fourth volume of this well-known series are: Determination of Organic Peroxides (A. J. Martin), Enzyme Analytical Reactions (John B. Neilands), Gas Chromatography (Stephan Dal Nogare and Leo W. Safranski), Application of Nuclear Magnetic Resonance Spectroscopy to Organic Analysis (Harlan Foster), Crystallographic Methods of Analysis: X-Ray Diffraction and Microscopy (John Krc, Jr.) and Application of Differential Thermal Analysis to High Polymers (Bacon Ke).

A glance at these titles will immediately reveal the character of this work—its keynote is diversity. We have here methods as old as chemistry itself (crystallography) and the very latest (NMR); specific (determination of peroxides) and specialised (enzyme) methods, and those capable of very

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broad applications (NMR, GPC). Thus users of this book will include those looking for specific procedures as well as those interested in surveying broader fields.

Although all of the sections are adequate and well-written, it seems clear to this reviewer that the one on Gas Chromatography is the outstanding contribution of this volume to the chemical literature. Written by two outstanding experts in the field, this treatment is a fine balance of theory, instrumentation and applications. Of special interest are the attention paid to special applications, and the very useful Table XVI which lists liquid phases and temperature ranges suitable for the separation of a variety of typical classes of compounds. A bibliography of 336 references puts the reader in easy access of the important original papers and monographs in the field.

The only section that seems to come off less than well is that on Crystallographic Methods. The reason is obvious: an attempt is made to cover the subjects of crystal optics, crystal morphology and X-ray diffraction in 30 odd pages—a patently impossible task. A reader with little previous experience in this area will learn little, except some terminology, from these pages. The portion on fusion methods is more useful.

The book is attractively bound and printed, and the few typographical errors noted were obvious ones (such as in the legend for fig. 2. p. 68). Finally, the volume has a rarity value. It is undoubtedly the only analytical chemistry work where one can learn where Mozart composed the music for "*Cosi fan tutte*".

ROBERT L. LITLE

Monographs on the Radiochemistry of Elements. The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

THIS is a series of monographs on the radiochemistry of the elements. Each monograph is written by an authority on the radiochemistry of the particular element, and has been written to a standard format. Contents include general reviews of the inorganic, analytical and radio-chemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

The major part of the monograph is taken up by the last section, and a critical selection of the known radiochemical techniques for each element has obviously been made. A number of the procedures have originated in Atomic Energy Establishments and it is possible that their appearance in these monographs marks their first open publication. The literature has, in some of the monographs, been covered up to 1960.

This series will be of particular interest to the radiochemist or the analytical chemist. It will also be of value to the biochemist and the physicist who often use radiochemical techniques in the solution of specific problems.

The most recent monographs in the series now available are:—

NAS–NS–3010 **The Radiochemistry of Barium, Calcium and Strontium.** D. N. SUNDERMAN and C. W. TOWNLEY. January 1960. $1.25.

3011 **The Radiochemistry of Zirconium and Hafnium.** E. P. STEINBERG. January, 1960. $0.50.

3013 **The Radiochemistry of Beryllium.** A. W. FAIRHALL. May 1960. $0.75.

3014 **The Radiochemistry of Iridium.** D. N. SUNDERMAN and C. W. TOWNLEY. May 1960. $0.50.

3015 **The Radiochemistry of Zinc.** H. G. HICKS. June 1960. $0.75.

3016 **The Radiochemistry of Protactinium.** H. W. KIRBY. December 1959. $1.00.

3017 **The Radiochemistry of Iron.** J. M. NIELSEN. August 1960. $0.50.

3018 **The Radiochemistry of Manganese.** G. W. LEDDICOTTE. October 1960. $0.50.

3020 **The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium.** P. C. STEVENSON and W. E. NERVIK. Februrary 1961. $3.00.

3021 **The Radiochemistry of Technetium.** E. ANDERS. November 1960. $0.50.

3023 **The Radiochemistry of Tin.** W. E. NERVIK. October 1960. $0.50.

3024 **The Radiochemistry of Magnesium.** A. W. FAIRHALL. January 1961. $0.50.

3025 **The Radiochemistry of the Rare Gases.** F. F. MOMYER, JR. October 1960. $0.75.

3026 **The Radiochemistry of Mercury.** J. ROESMER and P. KRUGER. December 1960. $0.50.
3027 **The Radiochemistry of Copper.** F. F. DYER and G. W. LEDDICOTTE. April 1961. $0.75.
3028 **The Radiochemistry of Rhenium.** G. W. LEDDICOTE. April 1961. $0.50.

In the same series the following publication has now appeared:—

Publication 825—**Source Material for Radiochemistry** (1st Revision) July 1960. This is an attempt to list current source material of interest to the radiochemist. It includes books on radiochemistry, nuclear chemistry, nuclear physics, collection of radiochemical procedures, references on ion-exchange and solvent extraction, activation analysis, nuclear geochemistry, counting techniques, nuclear data compilations, and even references on laboratory design and safety. It has undoubtedly something for every radiochemist or analytical chemist and it can be obtained, free of charge, from the Division of Physical Sciences, National Research Council, National Academy of Sciences, 2101, Constitution Avenue, Washington 25, D.C.

R. J. MAGEE

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung. Herausgegeben von der Fachgruppe Wasserchemie in der Gesellschaft Deutscher Chemiker, 3rd Edition. Verlag Chemie, Weinheim, 1960. Pts. 1 and 2, DM 27.50.

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THIS is the second part of the third new and enlarged edition of the German standard methods of examination of waters *etc.* (For a review of Part 1, see Talanta 1960, **5**, 291.) Colorimetric methods are given for the determination of nitrite and nitrate. Ammonia is determined by nesslerisation or titration, after distilling off the ammonia from a solution buffered at pH 7.4. The permanganate value is carried out with 0.01*N* $KMnO_4$ at the boil for 10 minutes. A full description is given of the procedure for estimating the Biochemical Oxygen Demand for periods of up to 20 days and the relationship which might be expected between the results and Permanganate Value is shown in tabular form. A method for the analysis of Organic Nitrogen is given. The longest section in this second part is devoted to the estimation of anionic synthetic detergents by the methylene blue method, or the formation of insoluble salts with *p*-toluidine hydrochloride, and the colorimetric estimation of cationic detergents, based on their formation of coloured compounds with bromophenol blue.

In the part dealing with the bacteriological examination of waters the recommendations of the World Health Organization regarding the frequency of examination in relation to the population supplied are given. This is followed by a description of standard procedures for determining the total count of bacteria, estimation of the number of coliform bacteria and E. coli. Concise instructions are given for the preparation and use of culture media. It is of interest that the membrane method of counting and identifying bacteria is described; the bacteria are filtered through a sterile membrane which is placed in sterile culture media so that the filtered bacteria grow to countable and identifiable colonies.

It is noted that no description has yet appeared for determining organic carbon, or phosphorus in its various forms. This book is recommended to all concerned with the examination of potable and polluted waters.

S. H. JENKINS

Talanta, 1961, Vol 8, pp. 764 to 767. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Assistant Editor).

BELGIUM

Tuesday–Friday 12–15 *June* 1962: **International Symposium on the Organic Chemistry of Natural Products:** organised by *Société Chimique de Belgique* on the occasion of the 75th anniversary of its foundation, under the auspices of I.U.P.A.C. Brussels.

The proceedings will be divided into 5 sections working simultaneously:

1. Structure of new natural Products.
2. Methods used for the determination of chemical structures.
3. Syntheses and chemical reactions (excluding degradation reactions).
4. Biosynthetic theories and their experimental verifications.
5. Mode of action of naturally occurring compounds in biological processes.

Section 2 is subdivided into:

(a) Analytical methods and chemical degradation.
(b) Physical methods.
(c) Stereochemical investigations (configurational and conformational).

Papers may be delivered in any language. Summaries, which should not exceed 200 words and should be written in one of the following languages: French, Dutch, English or German, must reach the Secretariat of the Symposium before 1st February, 1962.

Further information may be obtained from Professor A. BRUYLANTS, Chairman of Société Chimique de Belgique, c/o Fédération des Industries Chimiques de Belgique, 32, rue Joseph II, Bruxelles 4, Belgium.

FRANCE

Wednesday 25 *April–Friday* 4 *May* 1962: **Sixth Salon International de la Chemie** and **Conférence Internationale des Arts Chimiques.** Paris.

The Conférence Internationale des Arts Chimiques will include a series of scientific and technical meetings, including the **Journées Techniques de Paris** which will take place in the Maison de la Chimie. Subjects featured in the Journées Techniques de Paris will be:

Petroleum chemistry	Rubber
Plastics	Nuclear techniques
Paints, pigments and varnishes	Analytical tests
Measurement, control, regulation and automation	Alloy and special steels
Organic syntheses	Perfumery and cosmetics
Aerosols	Prevention of atmospheric pollution

Further information can be obtained from 28, rue Saint-Dominique, Paris VII^{e}.

Sunday–Saturday 26 *May–1 June* 1963: **Sixth International Mineral Processing Congress:** *la Société de l'Industrie Minérale*. Cannes.

This Congress will be concerned with all aspects of mineral processing and papers will be selected entirely on the basis of their scientific and technical value. However, particular emphasis will be placed on the following subjects:

1. The concentration of iron minerals, including magnetic roasting but excluding agglomeration.
2. Measurement, control and automation.
3. Hydrometallurgy.

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MEXICO

Tuesday–Friday 21 *November–1 December* 1961: **Radioisotopes in Animal Biology and Medical Sciences:** *International Atomic Energy Agency.* Mexico City.

UNITED KINGDOM

Wednesday 1 November 1961: Meeting for reading of **Original Papers:** *Society for Analytical Chemistry.* Burlington House, London, W.1. 7.00 p.m.

Thursday 2 *November* 1961: **Symposium on Electron Spin Resonance:** *Chemical Society.* Queen Mary College, London. 2.00 p.m.

Wednesday 8 *November* 1961: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 15 *November* 1961: **The Analysis of Finishes on Yarns and Fabrics:** Mr. E. MYTUM: *Society for Analytical Chemistry, Midlands Section.* Lanchester College of Technology, Coventry. 7.00 p.m.

Wednesday 15 *November* 1961: **Chemical Services on British Railways:** Dr. G. H. WYATT, F.R.I.C.: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, Newcastle and North-East Coast Section.* King's College, Newcastle. 6.30 p.m.

Wednesday 15 *November* 1961: **Recent Developments in Chromatography on Cellulose and Ion-exchange Cellulose:** Mr. N. F. KEMBER, A.R.I.C.: *Society for Analytical Chemistry, Scottish Section.* Royal Society of Edinburgh, George Street, Edinburgh. 7.15 p.m.

Friday-Saturday 17-18 *November* 1961: **Autumn Conference on Imperfections in Crystals:** *Institute of Physics and Physical Society, X-ray Analysis Group.* Institution of Mechanical Engineers, London.

Tuesday 21 *November* 1961: **Annual General Meeting** followed by **Retiring Chairman's Address:** *Society for Analytical Chemistry, Physical Methods Group.* Burlington House, London, W.1. 6.30 p.m.

Monday–Thursday 9–12 *April* 1962: **Feigl Anniversary Symposium:** *Society for Analytical Chemistry, Midland Section.* University, Edgbaston, Birmingham, 15.

This International Symposium on Analytical Chemistry will be held in honour of Professor F. Feigl to commemorate his 70th birthday. The programme will consist of:

(a) Contributions on original scientific work.
(b) Reviews of recent advances in selected branches of analytical chemistry.
(c) Exhibition of new scientific equipment.

Following the Symposium there will be a half-day Conference on the morning of Friday, 13 April, dealing with **The Teaching of Analytical Chemistry.** To this all delegates are invited.

The social programme will include a civic reception to the delegates and their ladies, a Symposium dinner, informal luncheons and dinners and a special programme arranged for lady visitors.

Plenary lectures will be given by Professor R. Belcher (U.K.), Professor F. Feigl (Brazil) and Professor P. W. West (U.S.A.).

To date the following lecturers have agreed to contribute:

R. BELCHER	U.K.	A. C. MENZIES	U.K.
E. W. BERG	U.S.A.	G. W. C. MILNER	U.K.
J. BERGER	Denmark	F. L. MOORE	U.S.A.
T. S. BURKHALTER	U.S.A.	L. OTTENDORFER	Austria
J. K. CARLTON	U.S.A.	J. W. ROBINSON	U.S.A.
F. CLANET	France	A. A. SMALES	U.K.
C. DUVAL	France	S. VEIBEL	Denmark
G. V. M. DUYCKAERTS	Belgium	A. WALSH	Australia
F. FEIGL	Brazil	H. F. WALTON	U.S.A.
H. FREISER	U.S.A.	H. WEISZ	Germany
L. GORDON	U.S.A.	F. WELCHER	U.S.A.

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I. M. KOLTHOFF	U.S.A.	P. W. WEST	U.S.A.
H. A. LAITINEN	U.S.A.	C. L. WILSON	U.K.
R. J. MAGEE	U.K.	P. ZUMAN	Czechoslovakia
H. MALISSA	Austria	J. ZYKA	Czechoslovakia

Applications forms and further information can be obtained from the Honorary Symposium Secretary: Mr. M. L. RICHARDSON, c/o John & E. Sturge Ltd., Lifford Chemical Works, Lifford Lane, Kings Norton, Birmingham 30, England.

The purpose of *NLL News*, a bulletin to be issued as occasion demands by the **National Lending Library for Science and Technology**, will be to inform potential users of the services which are available. The first issue describes the National Lending Library buildings at Boston Spa, Yorkshire, then deals briefly with what literature is available, how to obtain it, some notes on the loan service, and the London area office.

The following New British Standard is announced by B.S.I. News: *B.S. 3406: The determination of particle size of powders: Part I: 1961: Sub-division of gross sample down to 0·2 ml.* This describes methods of sub-division of gross samples of particulate material in preparation for determination of particle size for the purpose of size analysis by methods described in other parts of the standard. The total range covered is from 1,500 litre to 0·2 ml. Simple methods such as halving and coning and quartering are first described; then mechanical sub-dividers of the turntable and of the slotted cone type which are preferred as being faster and more accurate. For further sub-division below 1 litre, the grid type and the oscillating hopper type dividers are described. (Price 6s.)

B.S.I. News also announces the following Revised British Standard: *B.S. 1647: 1961: pH scale.* This applies to aqueous solutions at temperatures between 0 and 95°. The difference in pH between two solutions is defined in terms of a specified electrometric measurement, and the definition of pH is completed by assigning a value of pH at each temperature to one chosen solution (the primary standard). This primary standard is a 0·05 molar solution of pure potassium hydrogen phthalate. The solution is intended to ensure that, when different workers refer to a stated measured value of pH, they mean the same thing within ±0·005. Within this degree of accuracy there is no practical difference between the British Standard pH scale and the scale adopted by the National Bureau of Standards (U.S.A.). The standard includes recommendations on the use and calibration of the glass electrode, and pH values of aqueous solutions suitable for this purpose. (4s.6d.)

The following Amendment Slips are announced:

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 8: 1959: Chlorine in coal. Amendment No. 1: PD 4185.

Addendum 1: 1960 to B.S. 2690: 1956: Methods of testing water used in industry. Amendment No. 1: PD 4211.

B.S. 2782: Methods of testing plastics: Part 4: 1958: Analytical methods and viscosity in solution. Amendment No. 5.

Methods 402: Analysis of water extract of phenolic mouldings. PD 4214.

B.S. 3278: General recommendations for the sampling of imported iron ores: Part I: 1960: Hammer and shovel method. Amendment No. 1. PD 4178.

UNITED STATES OF AMERICA

Monday 30 *October–Wednesday* 1 *November* 1961: **Annual Meeting of Association of Official Agricultural Chemists.** Shoreham Hotel, Washington, D.C.

Amongst other materials, papers will be presented relating to the analysis of antibiotics, beverages, carbohydrates, colours, cosmetics, drugs, feeds, fertilizers, flavours, foods, fruits, oils, pesticides, radioactivity, vegetables and vitamins.

Further details are available from the Association of Official Agricultural Chemists, Inc., Box 540, Benjamin Franklin Station, Washington 4, D.C.

Wednesday–Friday 1–3 *November* 1961: **Annual Pittsburgh Diffraction Conference:** *Mellon Institute*. Mellon Institute, Pittsburgh.

Thursday–Friday 2–3 *November* 1961: **Tenth Instrumentation Conference.** Louisiana Polytechnical Institute.

Monday–Wednesday 6–8 *November* 1961: **Atomic Industrial Forum Annual Conference.** Conrad Hilton Hotel, Chicago, Ill.

Monday–Thursday 6–9 *November* 1961: **Atom Fair Exhibit.** Conrad Hilton Hotel, Chicago, Ill.

Tuesday–Thursday 7–9 *November* 1961: **American Nuclear Society Annual Meeting.** Conrad Hilton Hotel, Chicago, Ill.

Wednesday–Friday 15–17 *November* 1961: **1961 Eastern Analytical Symposium and Instrument Exhibit.** Statler Hilton Hotel, New York City. (See also *Talanta*, 1961, **8**, 691).

Monday–Friday 27 *November–1 December* 1961: **Twenty-Eighth Exposition of Chemical Industries.** The Coliseum, New York City.

An authoritative reference work on food additives is to be prepared jointly over a five year period by the Food Protection Committee, National Academy of Sciences—National Research Council and the Toxicology Study Section, National Institutes of Health with some financial help from the U.S. Department of Health, Education and Welfare. The *National Food Chemicals Codex*, as the volume will be known, will be similar to the *U.S. Pharmacopeia and National Formulary* and will set forth methods of analysis and standards of identity and purity of chemicals used as intentional additives in foods. The project will be directed by Dr. JUSTIN J. POWERS.

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Talanta, 1961, Vol. 8, p. 768. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Analysis of gases and vapours by spectroscopic techniques—I: Emission spectroscopy: W. D. McGrath, R. J. Magee, W. F. Pickering and C. L. Wilson. (20 *July* 1961).

Analysis of gases and vapours by spectroscopic techniques—II: The absorption spectra of gases and vapours: W. D. McGrath, R. J. Magee, W. F. Pickering and C. L. Wilson. (20 *July* 1961).

Analysis of gases and vapours by spectroscopic techniques—III: Applications of electronic absorption spectra: W. D. McGrath, R. J. Magee, W. F. Pickering and C. L. Wilson. (20 *July* 1961).

The determination of tantalum, niobium and titanium by homogeneous precipitation: R. Dams and J. Hoste. (22 *August* 1961).

Tetramethylguanidine—A new solvent for titration of weak acids: Theodore R. Williams and Jack Custer. (22 *August* 1961).

Improved electrodes for the continuous measurement of sodium and potassium: H. D. Portnoy, L. M. Thomas and E. S. Gurdjian. (22 *August* 1961).

Die Bestimmung kleiner Fluormengen—II: Roman Valach. (23 *August* 1961).

Spectrophotometric determination of palladium with didodeceyldithio-oxamide: William D. Jacobs, Clara M. Wheeler and William H. Waggoner. (23 *August* 1961).

The determination of interstitial elements in the refractory metals: Manley W. Mallett. (23 *August* 1961).

Precipitation of metal *8*-hydroxyquinolates from homogeneous solution V—magnesium: James T. Corkins, Richard F. Pietrzak and Louis Gordon. (23 *August* 1961).

Applications of infrared spectroscopy—VI: D. M. W. Anderson. (23 *August* 1961).

The complexometric determination of plutonium in reactor fuel processing plant solutions—I. Nitric acid solutions of irradiated uranium: D. G. Boase, J. K. Foreman and J. L. Drummond. (1 *September* 1961).

The regeneration of spent magnesium perchlorate desiccant: G. Frederick Smith. (1 *September* 1961).

The flame photometric determination of lead in lead alloys: C. L. Chakrabarti, R. J. Magee, W. F. Pickering and C. L. Wilson. (4 *September* 1961).

An automatic-recording titration apparatus for use with slow reactions: L. R. Leake and G. F. Reynolds. (4 *September* 1961).

Analytical aspects of the oxidation of organic nitrogen compounds with chromic acid: M. Jurecek, V. Novak and P. Kozak. (4 *September* 1961).

Azofarbstoffe als Reagenzien zur spektrophotometrischen Bestimmung von UranIV, VI und Thorium in Losungsmittelgemischen: G. E. Janauer und J. Korkisch. (8 *September* 1961).

Photometric titrations—VI: The determination of submicrogram quantities of calcium and magnesium: H. Flaschka and P. Sawyer. (10 *August* 1961).

Talanta, 1961, Vol. 8, pp. 769 to 774. Pergamon Press Ltd. Printed in Northern Ireland

SOME THEORETICAL AND PRACTICAL PROBLEMS IN THE USE OF ORGANIC REAGENTS IN CHEMICAL ANALYSIS—I

EFFECT OF DONOR π BONDS ON THE STABILITY OF CHELATE COMPLEXES CONTAINING SULPHUR

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Institute of Inorganic and Analytical Chemistry, L. Eötvös University of Budapest, VIII, Múzeum-körút 4/b, Hungary

(*Received* 12 *June* 1961. *Accepted* 17 *July* 1961)

Summary—The effect of the donor π bonds on the stability of chelate complexes has been investigated. It has been shown that the stability of chelates which contain sulphur as a donor atom shows a marked dependence on the effect of the donor π bond. On the basis of theory it is possible to explain the optimum pH range for the analytical use of dithizone.

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IN the formation of complexes one must consider, in addition to the conventional co-ordinate bonds, the possibility of the formation of donor π bonds by certain metals. In such cases *d* electrons are delivered by the metal to a free *d* or *p* orbital of the ligand. The delivery of an electron raises the electron affinity (electrophilic nature) of the metal, thus increasing the attacking power of nucleophilic ligands, *i.e.*, the strength of the σ bond between the metal and the ligand.

The role of donor π bonds in complex chemistry was first pointed out by Pauling,[1] Philips,[2] Chatt[3] and Dewar.[4] Recently, a number of authors[5–9] have emphasised that the formation of a donor π bond leads to an increase in the stability of the complex. So far, in the field of chelate complexes, no investigations of this type are known, although it would be possible to interpret several anomalies on the basis of this phenomenon.

The object of the present study was to investigate the occurrence and the effect of the donor π bond in the complexes of chelate-forming agents which contain sulphur as one of the donor atoms, and to examine the field of application of molecules of this type (in the present paper dithizone) as organic reagents.

The prerequisites for the formation of a donor π bond are as follows:

(1) The presence of free *d* electrons among the valence electrons of the central metal atom is essential. With increase in the number of *d* electrons, the probability of formation of π bonds becomes higher.

(2) A free *d* or *p* orbital capable of accepting an electron from the central atom must be present in the external electron shell of the donor atom of the ligand.

(3) A stable σ bond must exist between the central atom and the ligand.

According to existing information, the following cations are capable of forming donor π bonds: Cu^{+}, Ag^{+}, Au^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{2+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Pd^{2+}, Pt^{2+} and Pt^{4+}*. Of the ligands acting as chelate-forming agents, molecules which contain sulphur, selenium, phosphorus or arsenic

* The formation of donor π bonds can also be presumed in the case of other metals to a lesser extent.

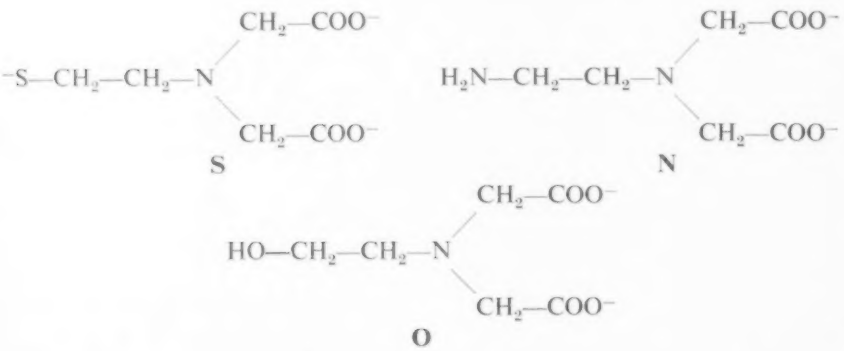
as donor atoms are capable of forming bonds of this type, in contrast to those which contain nitrogen* or oxygen as donor atoms.

The anomalies connected with the stability and the chemical behaviour of chelate complexes containing sulphur as a donor atom can be interpreted in the following way.

I. The stability exponents of the metal complexes of the following three compounds prepared by Schwarzenbach[11] are presented in Table I.

TABLE I

Metal ion	1 pK_S	2 pK_N	3 pK_O
Mn^{2+}	9·32	7·71	5·55
Fe^{2+}	11·72	9·81	6·78
Co^{2+}	14·67	11·78	7·90
Ni^{2+}	13·75	13·73	9·28
Cu^{2+}	—	15·90	11·86
Zn^{2+}	15·92	11·93	8·93



The possibility of the formation of a donor π bond is only present in the molecule S.

The data of Table I prove that the rule derived by Irving and Williams[10] does not hold in the case of complexes containing a donor π bond. In column 1, the zinc complex shows the greatest stability in the series Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}.

On the basis of the crystal field theory the validity of this rule depends on the spin-paired or spin-free state (more exactly low spin-number or high spin-number) of the central atom of the complex. In the case of paired spin arising from the change in electron configuration, the Irving-Williams rule does not hold. As was pointed out in the introduction, if a strong donor π bond exists, the σ bond is also stronger, so that the crystal field energy of the ligands is great, favouring the formation of spin-paired complexes. In the complexes with a strong donor π bond the anomaly in the Irving-Williams rule can be interpreted. The existence of the donor π bond

* Owing to their capacity for forming donor π bonds, the oximes occupy a particular place among the chelate-forming agents which contain nitrogen as a donor atom. This problem will be discussed in a subsequent paper.

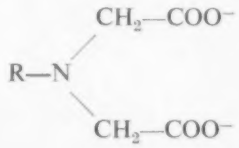
TABLE II

Metal ion	1 pK_O–pK_N	2 pK_S–pK_O	3 pK_{S-N}	4 pK_{S-O}
Mn^{2+}	1·51	3·77	1·6	2·1
Fe^{2+}	1·91	4·94	1·9	3·1
Co^{2+}	2·89	6·77	2·9	4·8
Ni^{2+}	—	4·47	—	2·4
Cu^{2+}	—	—	—	—
Zn^{2+}	3·99	7·59	4·1	5·8

does not mean in all cases a stability of an order which deviates from the Irving-Williams rule. There is no doubt, however, that the stronger the donor π bond that can be formed, the greater is the probability of the Irving-Williams rule being invalid.

The stability exponent values published by Schwarzenbach enable us to calculate the increase of stability caused by the donor π bond for the complexes shown in Table I.

Taking into account the analogous nature of the three molecules, and the identical structure of the complexes formed, the differences, $pK_S - pK_N$ and $pK_S - pK_O$, in the stability exponents denote the increase in stability caused by the replacement of the donor atoms, nitrogen and oxygen, respectively, by sulphur (Table II, columns 1 and 2). Since the substitution of a sulphur atom changes the acidic dissociation constant of the molecules (particularly in the case of oxygen) this fact must also be considered when establishing the stability increase caused by the donor π bond. In the case of the analogues of



(where the group R did not contain any donor atoms and only altered the acidic dissociation constant of the compound), the stability constants of the complexes were plotted by Schwarzenbach[11] against their acidic dissociation constants. Stability increases caused by the co-ordination of the fourth donor atom, (sulphur in the case of compound S, where $R = {}^{-}S{-}CH_2{-}CH_2$; nitrogen in the case of compound N, where $R = H_2N{-}CH_2{-}CH_2$; and oxygen in the case of compound O, where $R = HO{-}CH_2{-}CH_2$), were characterised by the distance of the experimentally determined stability constants from the curve in Schwarzenbach's diagram, measured on the ordinate (in terms of pK). From these data, the stability increase resulting from the formation of the donor π bond was calculated (Table II, columns 3 and 4). The values in columns 1 and 3 are approximately identical. This may be ascribed to the fact that the acidic dissociation constants of the compounds S and N are almost the same ($pK_H = 10{\cdot}79$ for S, $pK_H = 11{\cdot}05$ for N, but $pK_H = 8{\cdot}73$ for O). Thus, the stability increase is almost exclusively caused by the donor π bond.

On considering the identical structure of all three complexes (identical ring number, *etc.*), the stability increase (rise of free energy of formation) may be ascribed to the change of enthalpy. The entropy factor remained unchanged. The change of

enthalpy resulting from the formation of the donor π bond can be calculated from the formula

$$-RT \ln \Delta K = \Delta H^{\circ}.$$

II. The marked differences between the stabilities of the chelate complexes of metals containing 18 electrons in the external electron shell and of those of metals with 18 + 2 electrons when they contain sulphur as the donor atom can be explained by the formation of a donor π bond. In the latter case, the *d* electrons of the metal are incapable of occupying the free *d* orbital of sulphur. In this way, it is possible to interpret the differences in the stabilities of the ketodithizonate complexes of Hg^{2+} and Pb^{2+}, and in those of Cd^{2+} and Sn^{2+} (Table III).

TABLE III

Metal ion	Electron orbitals	Stability exponent of ketodithizonate	Ref.
Hg^{2+}	$5s^2,5p^6,5d^{10}$	44·15	12
Pb^{2+}	$5s^2,5p^6,5d^{10}:6s^2$	18·66	13
Cd^{2+}	$4s^2,4p^6,4d^{10}$	19·54	13
Sn^{2+}	$4s^2,4p^6,4d^{10}:5s^2$	15·34	12

III. In the case of metals with an identical external electron shell structure, the strength of the donor π bond depends on the mobility of the *d* electrons. The mobility of the electrons participating in the formation of a π bond can be characterised by the energy required for the further ionisation of the metal ion in question (in the case of bivalent metals by the third ionisation potential). The lower this value, the more stable is the donor π bond. To prove this statement, the stability exponents of the complexes of the compounds of Schwarzenbach[11] denoted as S, N and O, formed with Zn^{2+}, Cd^{2+} and Hg^{2+} ions, are presented in Table IV, together with the stability exponents of the ketodithizonates of Cd^{2+} and Hg^{2+}. Although it would also be possible to interpret the differences of stability (particularly in the case of the complexes of Cd^{2+} and Hg^{2+}) by the Fajans theory of polarisation, the change of the order of stability values in the case of the compound S supports the postulated effect of the donor π bond.[21]

TABLE IV

Metal ion	Ionisation potential ($Me^{2+} - e \rightarrow Me^{3+}$)	Chelating agent (Donor atom, S)	Stability exponent	Chelating agent (Donor atom, N)	Stability exponent	Chelating agent (Donor atom, O)	Stability exponent
Cd^{2+}	37·766	dithizone	19·54	—	—	—	—
Hg^{2+}	34·210	dithizone	44·15	—	—	—	—
Zn^{2+}	39·701	S	15·92	N	11·93	O	8·33
Cd^{2+}	37·766	S	16·72	N	10·58	O	7·52
Hg^{2+}	34·210	S	16·16	N	9·75	O	5·48

IV. On the formation of the donor π bond, the positive charge of the central atom increases slightly, because of a partial release of electrons. In the case of ions of identical electron shell, the probability of formation of π bonds decreases with the increase of the positive charge on the ion. A higher charge on the cation obviously reduces the mobility of the external *d* electrons. Thus, ligands capable of forming donor π bonds tend to stabilise the lower valence state of metals.*

* It was pointed out by Fischer[15] that Au^{I} is present in gold dithizonate.

On the basis of the theory of donor π bonds presented above, it is possible to explain the optimum pH range for the analytical use of organic reagents containing sulphur (particularly of dithizone). The greater the capacity of a metal cation, for forming donor π bonds the more stable will be its complex, and the lower will be

TABLE V. OPTIMAL PH RANGE FOR THE EXTRACTION OF METAL DITHIZONATES[19]

Metal ion	Metal:Dithizone	Electron orbitals	Ionisation potential ($Me^{n+} - e \rightarrow Me^{(n+1)+}$)	pH range
Ag^{+}	1:1	$4s^2$, $4p^6$, $4d^{10}$	21·481	−1·2–7
Hg^{2+}	1:2	$5s^2$, $5p^6$, $5d^{10}$	34·210	−1·4–4
Pd^{2+}	1:2	$4s^2$, $4p^6$, $4d^8$	32·921	−1·2–4
Pt^{2+}	1:2	$5s^2$, $5p^6$, $5d^8$	28·55	−1·2–4
Cu^{2+}	1:2	$3s^2$, $3p^6$, $3d^9$	37·079	+1·9–5
Bi^{3+}	1:3	$6s^2$		2·0–10
In^{3+}	1:3	$4s^2$, $4p^6$, $4d^{10}$	57·8	4·0–6·5
Sn^{2+}	1:2	$5s^2$		4·9–9·0?
Zn^{2+}	1:2	$3s^2$, $3p^6$, $3d^{10}$	39·701	6·0–9·4
Cd^{2+}	1:2	$4s^2$, $4p^6$, $4d^{10}$	37·766	6·0–14·3
Co^{2+}	1:2	$3s^2$, $3p^6$, $3d^7$	33·491	6·0–8·0
Ni^{2+}	1:2	$3s^2$, $3p^6$, $3d^8$	35·165	6·0–8·5
Pb^{2+}	1:2	$6s^2$		7·0–10
Fe^{2+}	1:2	$3s^2$, $3p^6$, $3d^6$	30·643	7·3–9·5
Mn^{2+}	1:2	$3s^2$, $3p^6$, $3d^5$	33·690	9·5–10·5
Tl^{+}	1:1	$6s^2$		

the pH range where its ketodithizonate is suited for use (Table V).* Accordingly, the entirely empirical Wichmann rule[16] loses its validity.†

The effect of the donor π bond on the stability of ketodithizonates proves, in accordance with the experiments of Irving[17] and Geiger,[18,19] and in contrast with the opinion of Fischer,[20] that the sulphur atom of dithizone participates in the formation of complexes as a donor.

Zusammenfassung—Der Effekt der Donor-π-Bindung auf die Stabilität von Chelatkomplexen wird studiert. Es wird gezeigt, dass die Stabilität von Chelaten, die Schwefel als Donoratom enthalten, durch diesen effekt erhöht wird. Auf der Basis der Theorie ist es möglich den optimalen pH-Bereich für die analytische Anwendung von Dithizon zu interpretieren.

Résumé—L'auteur a étudié l'influence de la liaison π d'un donneur sur la stabilité des complexes chelatés. Il a montré que la stabilité des chélates, qui contiennent du soufre comme atome donneur, dépend de l'action de la liaison π du donneur. En se basant sur la théorie de cette liaison, il est possible d'interprêter le domaine de pH le meilleur pour l'utilisation analytique de la dithizone.

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* The number of rings (ratio of metal to dithizone), the configuration of the external electron shell, and the corresponding ionisation potentials are presented in Table V as factors determining the stability.

† The nobler the metal component of the dithizonate the lower is the pH value of extractability (Wichmann).

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ISOTOPIC DILUTION ANALYSIS BY ION-EXCHANGE—I.

DETERMINATION OF TRACES OF IRON

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Summary—Isotopic dilution analysis with the use of ion-exchangers serves for the determination of trace amounts of metals. A theoretical evaluation of this method is given, from which the conditions for the determination of a number of metals can be predicted. The selectivity of the method may be further increased by the use of masking and precipitating agents.

The proposed method has been verified by the determination of iron using EDTA and Dowex 50 cation-exchanger. The average precision of mean values for amounts of 10^{-7} g of Fe/5 ml was 1·2%, for amounts of 10^{-8} g of Fe/5 ml, 4·0% and for amounts of 10^{-9} g of Fe/5 ml, 4·1%. Even a large excess of many metals does not interfere in the analysis. The method has been applied to the analysis of NaI(Tl) crystals. The procedure which has been developed is very simple, and is far more sensitive than colorimetry, activation analysis or other methods used up to now for determining traces of iron.

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INTRODUCTION

IN previous papers,[1,2,3] it has been shown that isotopic dilution analysis can be used for the determination of trace amounts of an element, if the following conditions are fulfilled: (1) a radio-isotope having a suitable half-life period and high specific activity (or a carrier-free isotope) is available, (2) it is possible to isolate very small, equal amounts of the analysed element from solutions containing it in different amounts. The second condition can be fulfilled by adding equal amounts of a complexing agent to the analysed solutions. The amount of the reagent added must, however, be less than the amount which corresponds stoichiometrically to the element present. The complex which is formed is separated from the excess of the element analysed by solvent extraction (see previous papers[1,2,3]), ion-exchange (this paper), partition chromatography, electrophoresis, electrolysis, *etc.*

In the present paper, general relations have been derived, on the basis of which it is possible to calculate the conditions for the determination of a number of elements by this method. Using suitable masking or precipitating agents it is possible to obtain increased selectivity for the proposed method. The method has been tested by the determination of trace amounts of iron (from 10^{-7} to 10^{-9} g/5 ml) in the presence of an excess of many elements, using EDTA and the cation-exchanger Dowex 50.

THEORETICAL

For the isolation of very small, equal amounts of the ion to be determined from solutions containing various amounts of this ion, it is necessary that the following conditions should be fulfilled: (1) the amount of complexing agent added must be less than corresponds stoichiometrically to the amount of ion present, (2) the complexing agent must react quantitatively with the ion, (3) the complex formed must be easily separable from the excess of the analysed metal. In order that more than

99·9% of the complexing agent H_nY should react to form the complex MY,* the following relation must be valid:

$$[MY] > 0{\cdot}999\, c_{H_nY} \tag{1}$$

where c_{H_nY} is the initial concentration of the complexing agent. The equilibrium concentration of the metal M is given by:

$$[M] = c_M - [MY] = c_M - c_{H_nY} \tag{2}$$

where c_M is the initial concentration of the metal. The equilibrium concentration of the anion Y is calculated from the relation:

$$\sum_{n=0} [H_nY] = [Y] \sum_{n=0} \frac{[H]^n}{k_0 \ldots k_n} \leqslant 0{\cdot}001\, c_{H_nY} \tag{3}$$

where

$$k_n = \frac{[H] \,.\, [H_{n-1}Y]}{[H_nY]} \text{ and } k_0 = 1. \tag{4}$$

By inserting the relations (1), (2) and (3) into the expression for the stability constant of the metal complex, K_{MY}, we obtain:

$$K_{MY} = \frac{[MY]}{[M]\,[Y]} > \frac{c_{H_nY}}{c_M - c_{H_nY}} \,.\, \frac{\sum_{n=0} \frac{[H]^n}{k_0 \ldots k_n}}{0{\cdot}001\, c_{H_nY}} \,. \tag{5}$$

From relation (5) it may be seen that the term $\frac{c_{H_nY}}{c_M - c_{H_nY}}$ has no great influence on the required value of K. At $c_M > 2\, c_{H_nY}$, this term will be < 1. Also the term $\sum_{n=0} \frac{[H]}{k_0 \ldots k_n}$ will be equal to 1 at sufficiently high pH-values (*i.e.*, at a pH-value at which the complexing agent will be completely dissociated). For the determination of trace amounts of metals ($c_{H_nY} \leqslant 10^{-5} M$) it will therefore be possible to use only those complexes for which $K_{MY} > 10^8$. This condition is fulfilled by the complexes of practically all metals with ethylenediaminetetra-acetic acid, 1,2-diaminocyclohexanetetra-acetic acid, *etc.*[4,5] For instance the value of $K_{FeY} = 10^{25{\cdot}1}$. It follows from relation (5) that iron^{III} can be determined by this method at pH 2 to 3, when hydrolysis is not yet measurably evident, even when using very low EDTA concentrations ($\sim 10^{-8} M$). The use of complexones has the advantage that the complexes formed are either neutral or negatively charged, so that they can be very easily separated from the excess of positively charged ions of the element being determined by the use of ion-exchange, paper chromatography, electrophoresis, *etc.*

From the stability constants of the various complexes it is also possible to determine the influence of interfering ions:

$$\frac{[M'Y]}{[M''Y]} = \frac{K_{M'Y}\,[M']}{K_{M''Y}\,[M'']} \,. \tag{6}$$

When [M″] is equal to [M′], it is possible to determine [M′] in the form of the complex M′Y, when $\frac{K_{M'Y}}{K_{M''Y}} > 10^3$, for [M″] = 100[M′] the value of $\frac{K_{M'Y}}{K_{M''Y}}$ must be $> 10^5$, *etc.*

* For the sake of simplicity the magnitude of the charges has been omitted.

For instance, in the determination of iron^{III} in the form of a complex with ethylenediaminetetra-acetic acid, no interference will be observed from most uni- or bi-valent metals, because for these the relation $\frac{K_{FeY}}{K_{M''Y}} > 10^5$ holds.[4] The metal which forms the strongest complex with a certain reagent can therefore be determined even in the presence of most other metals. By the use of masking agents which form complexes MB_n with the interfering metals (the masking agent may also be the hydroxyl ion—forming hydroxy-complexes—ammonia, *etc.*), it is even possible to determine selectively a number of other metals. In the presence of a masking agent the total concentration of the metals is:

$$c_M = [M] + [MY] + [MB_n] = [M]\,[1 + K_{MY}[Y] + K_{MB_n}[B]^n] \tag{7}$$

where

$$K_{MB_n} = \frac{[MB_n]}{[M]\,[B]^n}. \tag{8}$$

In this case:

$$\frac{[M'Y]}{[M''Y]} = \frac{K_{M'Y}[M'](1 + K_{M''Y}[Y] + K_{M''B_n} \cdot [B]^n)}{K_{M''Y} \cdot c_{M''}} \tag{9}$$

It may be seen from relation (9), that at high values of the term $K_{M''B_n} \cdot [B]^n$ it is possible to carry out the determination of the metal M′ even in the presence of an excess of the metal M″, which would otherwise interfere in the determination (the value $\frac{K_{M'Y}}{K_{M''Y}} < 1$). For instance, in the presence of chloride ions strong complexes are formed with Hg^{II} and Tl^{III}, and therefore even an excess of these elements does not interfere in the determination of iron^{III} in the form of a complex with ethylenediaminetetra-acetic acid, although the $K_{M''Y}$ values for these elements are close to the value of K_{FeY}.[4] To increase selectivity, precipitating agents may be used in a way similar to the masking agents. In this case:

$$\frac{[M'Y]}{[M''Y]} = \frac{K_{M'Y} \cdot S_{M'}}{K_{M''Y} \cdot S_{M''}} \tag{10}$$

where S_M is the solubility product. For instance, it would be possible to use diethanoldithiocarbaminate to mask metals of the first to third analytical groups when determining Ca and Sr in an ammoniacal medium, since $S_{Ca(Sr)} \gg S_{M''}$.

The use of dilution analysis also brings another advantage. This is the fact that after adding the radio-isotope to the solution being analysed, losses of the element being determined, occuring in further operations (when it is impossible to determine the element selectively in a single operation) do not influence the result of the analysis.

EXPERIMENTAL

Instruments

Scintillation counter with well-type NaI(Tl) crystal.
Set of 12 ion-exchanger columns, diameter 0·7 cm, height 10 cm.

Reagents

Twice distilled water: Further purified by passage through a column of ion-exchanger; used for dissolving all reagents, and for all other operations.

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HCl: Prepared by dissolving twice distilled gaseous HCl in water. The gaseous HCl was prepared from a mixture of HCl, AnalaR and H_2SO_4, AnalaR.

Disodium salt of EDTA: AnalaR

Ferric chloride: 120·85 mg of ferrum reductum, AnalaR, was dissolved in HCl, boiled with a few ml of H_2O_2, AnalaR, Merck, and made up to a volume of 1 litre. The solution thus prepared was diluted to the appropriate concentration by 0·01*N* HCl.

Ferric chloride: Tagged by ^{59}Fe. A solution of 500 mc/g was diluted to a suitable concentration using 0·01*N* HCl.

Cation-exchanger: Dowex 50 Wx in Na-form, 50/100 mesh, total capacity 5·2 ± 0·3 meq per dry g.

Preparation of the columns

The columns were filled with cation-exchanger Dowex 50 Wx and washed first 3 to 5 times with a solution of EDTA-disodium salt, then 3 to 5 times with water. This purification was repeated after each experiment.

Procedure

To 5 ml of a solution containing, in addition to iron^{III}, an excess of other metals, a precisely known amount, *y*, of radio-iron is added (see Table I) and 1 ml of a solution of EDTA-disodium salt of such concentration (Table I) that there is insufficient to correspond stoichiometrically to the iron present. The pH of the solution is brought to 2–3 by adding HCl. After allowing the solution to stand for 20–30 min at elevated temperature (30 to 40°) to permit the reaction of iron and EDTA to go to completion, the solution is passed through the cation-exchanger column at a rate of 0·3 ml/min. After washing the column with water the eluate is made up to 10 ml, and the activity of 3 ml of the eluate (A_2) is measured by a scintillation counter. A solution containing only radio-iron is treated in exactly the same way. The amount of radio-iron present in this solution need not be known precisely, but must, however, be more than stoichiometrically equivalent to the EDTA-disodium salt added. The amount of EDTA-disodium salt must be precisely the same as in the first case. After measuring the activity of 3 ml of the eluate (A_1), the amount of iron present, *x*, is calculated from the relation

$$x = y\left[\frac{A_1}{A_2} - 1\right]. \tag{10}$$

The results of the determination of iron in amounts of 10^{-7} to 10^{-9} g in 5-ml volumes are given in Table I.

The determination of traces of iron in sodium iodide

Traces of iron present in NaI crystals influence unfavourably their luminescent properties, which are made use of in scintillation techniques. For the determination of amounts of iron of the order of 10^{-3}–10^{-5} % by a colorimetric method, 10–20 g of the sample must be used.[6] A further increase in the sensitivity of the colorimetric methods is not possible. If, however, iron is separated by extraction with acetylacetone (to free it from excess NaI, and possibly some of the interfering metals) it is possible to determine as little as 10^{-7} % of iron in a 1-g sample.

Procedure

An amount of NaI between 0·1 and 1·0 g is dissolved in 5 ml of purified water, 1–5 ml of hydrogen peroxide are added and the solution is brought to the boiling point and evaporated till dry. To the residue 5 ml of water are added, the solution is boiled, and to the hot solution a known amount of radio-iron, *y*, is added. The pH of the solution is brought to 4–7 by adding a few drops of (twice distilled) ammonia, and the solution is extracted by 0·01*M*-acetylacetone in benzene. The organic phase is separated (a quantitative extraction of iron need not be carried out) and evaporated to dryness, to remove excess acetylacetone. To the residue 5 ml of 0·01–0·001*N* HCl are added and the required amount of EDTA-disodium salt, and the analysis is completed in the way already described.

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TABLE 1—DETERMINATION OF TRACES OF IRON

($1{\cdot}2 \times 10^{-7}$–$2{\cdot}4 \times 10^{-9}$ g of Fe/5 ml)

Iron taken, μg (X)	Active iron added, μg (y)	Activity of extracts[a] A_1	A_2	Iron found, μg (x)	Deviation from mean, μg Δ	Other metals present, μg	Deviation[b]
0·12085	0·04275	44350	11860	0·1171	−0·0052	10 Al^{3+}	$\sigma = 0{\cdot}1223$
		44350	11534	0·1216	−0·0007	0	$\delta = \pm 0{\cdot}0014 = \pm 1{\cdot}2\%$
		44350	11110	0·1279	+0·0056	10 Cd^{2+}	$\sigma - X = \pm 0{\cdot}0014 = \pm 1{\cdot}2\%$
		44350	11207	0·1264	+0·0041	10 Zn^{2+}	
		44350	11265	0·1256	+0·0032	10 Hg^{2+}	
		44350	11512	0·1219	−0·0004	10 Tl^{+}	
		40295	10650	0·1190	−0·0033	10 Ag^{+}	
		40295	10670	0·1187	−0·0036	10 Co^{2+}	
0·012085	0·021380	3693	2405	0·01145	−0·00108	1 Mn^{2+}	$\sigma = 0{\cdot}01253$
		3693	2420	0·01125	−0·00128	1 Cd^{2+}	$\delta = \pm 0{\cdot}00050 = \pm 4{\cdot}0\%$
		3693	2192	0·01464	+0·00211	1 Co^{2+}	$\sigma - X = \pm 0{\cdot}00044 = \pm 3{\cdot}6\%$
		3693	2415	0·01131	−0·00122	1 Cr^{3+}	
		3693	2210	0·01434	+0·00181	1 Pb^{2+}	
		3693	2383	0·01175	−0·00078	1 Ni^{2+}	
		5561	3561	0·01201	−0·00052	0	
		5561	3410	0·01348	+0·00095	1 Al^{2+}	
0·002417	0·010690	4034	3189	0·002831	+0·000010		$\sigma = 0{\cdot}002821$ c
		4034	3070	0·003356	+0·000535		$\delta = \pm 0{\cdot}000114 = \pm 4{\cdot}1\%$
		4034	3200	0·002786	−0·000035		$\sigma - X = \pm 0{\cdot}000404 = \pm 14\%$
		4034	3255	0·002558	−0·000263		
		4034	3200	0·002786	−0·000035		
		4034	3166	0·002930	+0·000109		
		4034	3150	0·002999	+0·000178		
		4034	3332	0·002251	−0·000570		

[a] In the range $1{\cdot}2 \times 10^{-7}$ g of Fe/5 ml, $C_{H_nY} = 1{\cdot}0 \times 10^{-6} M$; A_1, A_2, expressed in cp 5 min.
In the range $1{\cdot}2 \times 10^{-8}$ g of Fe/5 ml, $C_{H_nY} = 1{\cdot}0 \times 10^{-7} M$; A_1, A_2, expressed in cp 5 min.
In the range $2{\cdot}4 \times 10^{-9}$ g of Fe/5 ml, $C_{H_nY} = 1{\cdot}0 \times 10^{-7} M$; A_1, A_2, expressed in cp 10 min.

[b] $\sigma = \dfrac{\sum_{x=1}^{x=n} x}{n}$; $\delta = \pm \sqrt{\dfrac{\Sigma\Delta^2}{n(n-1)}}$

Together with the analysis of the sample a blank is run in precisely the same way. The amount of iron present in 1·00 g of NaI was found to be $3{\cdot}6 \times 10^{-7}$ g (mean of 3 measurements), *i.e.*, $3{\cdot}6 \times 10^{-5}$ %. The amount of iron in the blank was $0{\cdot}6 \times 10^{-7}$ g, (mean of 3 measurements) *i.e.*, $0{\cdot}6 \times 10^{-5}$ %.

DISCUSSION

From the results given in Table I, it follows that iron can be determined in amounts of $1{\cdot}2 \times 10^{-7}$ g/5 ml with an average precision of the mean value of 1·2%, in amounts of $1{\cdot}2 \times 10^{-8}$ g/5 ml with an average precision of 4·0% and in amounts of $2{\cdot}4 \times 10^{-9}$ g/5 ml with an average precision of 4·1%.

From stability constant values (see Theoretical) it may be expected that even a one hundred-fold excess of the following metals will not interfere in the determination of iron^{III} in the form of an EDTA complex: Tl^{+}, Ag^{+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, or Al^{3+}. The stability of the Cr^{3+}-EDTA complex is approximately the same[7] as for the Fe^{3+} complex; but since the Cr^{3+} complex is only formed in boiling solutions, even a one hundred-fold excess of chromium does not interfere in the determination of iron. Other metals which form very strong complexes with EDTA (*e.g.*, In^{3+}, Ga^{3+}, Bi^{3+}, Th^{4+}) interfere in the determination of iron. Contrary to what might be expected from the theory, a ten-fold excess of copper interferes in the determination of iron, even though the stability constant of the copper-EDTA complex is six orders of magnitude lower than that of the iron-EDTA complex. This effect may perhaps be interpreted as indicating that in passing through the column the original equilibrium of Fe-EDTA-Cu is shifted to the disadvantage of iron. The interfering effect of copper is eliminated only when the concentration of copper is lower than that of iron.

In conclusion, it must be mentioned that in the solution being analysed there should not be present a large excess of indifferent ions ($\geqslant 0{\cdot}1M$), which would lead to displacement of the adsorbed iron. Also there should not be present in the solution any complexing agents which would form negatively charged complexes with iron^{III}.

From a comparison of our results with literature data[8] it follows that the determination of iron by this method is more sensitive (maximum sensitivities of the various methods are given in brackets) than the determination by flame photometry (2×10^{-6} g/ml), by the graphite DC arc (2×10^{-7} g/ml), by the copper spark (5×10^{-7} g/ml), colorimetrically (5×10^{-8} g/ml) or by activation analysis (neutron flux 10^{13} neutrons. cm^{-2} sec^{-1}: $4{\cdot}5 \times 10^{-7}$ g/ml).

CONCLUSION

In the present paper a selective determination of traces of iron is described, in amounts of 10^{-7}–10^{-9} g/5 ml, carried out by the method of isotopic dilution analysis using ion-exchange. The proposed method may be used to determine trace amounts of a number of metals, and its sensitivity may be further increased by the use of carrier-free radio-isotopes.

Zusammenfassung—Isotopenverdünnungsanalyse in Verbindung mit Ionenaustauschern dient zur Bestimmung von Spurenmengen von Metallen. Theoretische Betrachtungen werden mitgeteilt und anhand der ableitungen lassen sich die optimalen Bedingung für die Bestimmung verschiedener Metalle voraussagen. Die Selektivität der Methode kann durch Anwedung von Maskierungs- und Fällungsmittel weiter gesteigert werden. Die vorgeschlagene Methode wurde anhand der Eisenbestimmung unter Verwendung von EDTA und Dowex 50 (Kationenaustauscher) getestet. Die mittlere Genauigkeit des Mittelwertes für Eisenmengen von 10^{-7} g Fe per 5 ml war 1·2%. Für 10^{-8} g

Fe per 5 ml 4·0% und für 10^{-9} g Fe per 5 ml 4·1%. Die Methode wurde zur Analyse von NaI(Tl) Kristallen herangezogen. Die entwickelte Methode ist recht einfach und wesentlich empfindlicher als Kolorimetrie, Aktivierungsanalyse oder irgendeineder anderen bisher entwickelten Methoden.

Résumé—L'analyse par dilution isotopique avec utilisation des échangeurs d'ions permet le dosage de traces de métaux. Les auteurs donnent la théorie de la méthode, d'après laquelle les conditions de dosage d'un certain nombre de métaux peuvent être prévues. La sélectivité peut être augmentée ultérieurement par l'utilisation d'agents complexants et de précipitation. La méthode proposée a été choisie pour le dosage du fer utilisant l'EDTA et la résine échangeur de cations Dowex 50. La précision moyenne des valeurs moyennes était: 1,2% pour des quantités de fer 10^{-7} g. pour 5 ml, 4,0% pour 10^{-8} g. de fer pour 5 ml et 4,1% pour 10^{-9} g. de fer pour 5 ml. Même un grand excès de nombreux métaux ne gêne pas l'analyse. La méthode a été appliquée à l'analyse de cristaux de NaI(Tl). La technique mise au point est très simple et beaucoup plus sensible que la colorimétrie, l'analyse par activation, ou toute autre méthode, utilisée jusqu'à maintenant, pour doser des traces de fer.

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CHELATOMETRIC DETERMINATION OF CYANIDE, THIOCYANATE AND CHLORIDE IN PRESENCE OF ONE ANOTHER

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Summary—A chelatometric method for the determination of cyanide, thiocyanate and chloride in the presence of one another is described. In one portion of the sample all three ions are precipitated by adding silver nitrate in excess. The silver precipitates are boiled with concentrated nitric acid. Silver chloride is not affected by this treatment while silver cyanide and thiocyanate are decomposed. The latter is oxidised to sulphate, the cyanide being expelled. The silver chloride precipitate is dissolved in a solution of potassium tetracyanonickelate and the liberated nickel is titrated with EDTA, the chloride content thus being determined indirectly. The sulphate solution after oxidation of thiocyanate is treated with a known volume of barium chloride solution and the excess of barium is titrated with EDTA solution of the same molarity. The difference between the volumes of barium chloride and EDTA solutions multiplied by a factor gives the thiocyanate content of the sample.

In a second portion of the sample, cyanide is determined by adding a known volume, in excess, of nickel sulphate solution and titrating the excess of nickel that has not combined with the cyanide. The difference between the volumes of the nickel and EDTA solutions multiplied by a factor gives the cyanide contents.

The method is rapid and accurate. A very small quantity of one of the components in the presence of large amounts of the others can be determined.

INTRODUCTION

THE classical titrimetric methods are too tedious for the separation and determination of cyanide, thiocyanate and chloride in the presence of one another. The chelatometric procedure described is rapid because use is made of the same operation for determining chloride and thiocyanate.

The principle of the chelatometric method is that silver chloride is not dissolved by hot nitric acid, while silver cyanide and thiocyanate are decomposed and dissolve, the latter being oxidised to sulphate. The silver chloride is filtered, washed, then dissolved in a solution of potassium tetracyanonickelate and the liberated nickel is titrated with EDTA,[1,2] thus determining the chloride content indirectly:

$$2AgCl + [Ni(CN)_4]^{2-} \rightarrow 2[Ag(CN)_2]^- + Ni^{2+} + 2Cl^- .$$

The sulphate contained in the filtrate is precipitated by adding a known volume, in excess, of barium chloride solution and the barium that has not precipitated is titrated, without filtering, with EDTA.[3,4] The difference in volumes of the barium and EDTA solutions (both solutions having the same molarity) multiplied by a factor gives the thiocyanate content.

Cyanide is determined in a separate portion of the sample by adding a known volume, in excess, of nickel sulphate[5] and the nickel that has not reacted in the formation of nickel tetracyanide is titrated with EDTA solution (both solutions having the same molarity). The difference between the volumes utilised, multiplied by a factor gives the cyanide content.

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EXPERIMENTAL

Reagents

Silver nitrate solution: 5% and 0·1%.

Nitric acid: Conc. and 1%.

0·1*M EDTA solution:* 37·21 g of disodium ethylenediaminetetra-acetic acid in 1 litre of water.

Saturated aqueous solution of murexide.

0·1*M Potassium tetracyanonickelate solution:* Prepared by titrating exactly 0·1 mole of nickel sulphate (in solution) after being made ammonial, with 1*M* potassium cyanide solution. The end-point is indicated when the solution changes from yellow to purple.

0·1*M Barium chloride solution:* The molarity of this solution should be adjusted exactly with that of the EDTA solution.

0·1% *Aqueous solution of metal phthalein* This should contain a few drops of ammonia solution.

Ammonia solution: Conc.

Sodium hydroxide solution: About 1*M*.

0·1*M Nickel sulphate solution:* The molarity of this solution should be adjusted exactly with that of the EDTA solution

Procedure

One g of the sample (or its equivalent of solution) is introduced into a beaker and 200 ml of water are added. An excess of 5% silver nitrate solution is poured slowly into the neutral solution and all three ions are precipitated. The suspension is warmed slightly, then allowed to stand. A little more 5% silver nitrate solution is added to the supernatant liquid to ensure that precipitation is complete. The precipitate is filtered on glass wool or asbestos, washed twice with 0·1% silver nitrate solution, then twice with 1% nitric acid.

The precipitate is transferred to a beaker and sufficient conc. nitric acid is added to cover the precipitate. The beaker is covered with a watch glass and the contents are boiled gently for 1 hr. More acid is added in case of rapid evaporation. The contents of the beaker are cooled, then water is added and the solution is filtered on a Gooch. Care must be taken not to use strong suction to avoid clogging of the filter. The silver chloride is washed twice with 0·1% silver nitrate solution, then twice with 1% nitric acid. The filter with the precipitate is transferred to a beaker containing sufficient potassium tetracyanonickelate solution for complete immersion of the precipitate. The contents of the beaker are stirred and warmed gently to aid solution.[6] As soon as the precipitate is dissolved, dilute the solution, add 1 ml of murexide solution and titrate slowly with EDTA to a yellow-to-purple end-point: 1 ml of 0·1*M* EDTA solution ≡ 7·091 mg of Cl^-.

The filtrate and the washings are collected in a beaker and brought to the boil. A known volume of 0·1*M* barium chloride solution, in excess, is added and the solution boiled for another 5 min so as to obtain a crystalline precipitate. The suspension is neutralised with approx. 0·1*M* sodium hydroxide solution, mixed with ethanol in the ratio of about 1:1, 5 ml of conc. ammonia solution added for every 100 ml of the mixture, followed by some drops of the indicator (metal phthalein) and the excess of barium titrated with 0·1*M* EDTA solution without delay: Each 1 ml difference in volume of 0·1*M* $BaCl_2$ and 0·1*M* EDTA solutions ≡ 5·808 mg of SCN^-.

To determine cyanide in the sample, 1 g is dissolved in water (or its equivalent of solution is taken), then a known volume of 0·1*M* nickel sulphate solution is added and some drops of murexide solution. The excess of nickel that has not combined with the cyanide is titrated with 0·1*M* EDTA solution: Each 1 ml difference in volume of 0·1*M* $Ni(SO_4)_2$ and 0·1*M* EDTA solutions ≡ 10·407 mg of CN^-.

RESULTS

The described method is rapid and makes use of very stable solutions. Some typical results obtained with artificially prepared samples are reproduced in Table I. The samples were prepared by mixing together accurately measured volumes of solutions of sodium chloride (1 ml ≡ 1 mg or 10 mg of Cl^-), sodium cyanide (1 ml ≡ 1 mg or 10 mg of CN^-), and sodium thiocyanate (1 ml ≡ 1 mg or 10 mg of SCN^-). The method is very satisfactory and works well even when a very small quantity of one of the components is in the presence of large amounts of the others.

TABLE I—SOME TYPICAL RESULTS OBTAINED WITH THE DESCRIBED METHOD

Taken, *mg*			Found, *mg*		
Cl^-	CN^-	SCN^-	Cl^-	CN^-	SCN^-
10	200	200	10·3	201·2	197·3
50	250	100	49·4	249·4	101·5
100	50	250	100·8	50·6	248·6
200	50	500	201·5	50·3	497·2
500	100	50	498·7	97·7	50·1
50	500	50	49·8	497·5	50·3
100	100	100	100·7	99·6	99·7
200	50	200	198·4	49·7	201·2
50	100	200	50·3	98·6	199·5
100	200	50	101·0	200·5	49·7
100	200	400	99·3	197·8	401·6
100	50	200	101·6	50·4	198·3

Zusammenfassung—Eine chelatometrische Methode zur Bestimmung von Cyanid, Rhodanid und Chlorid wird beschrieben. In einem Teil der Probe werden alle drei Ionen durch Zugabe von Silbernitrat gefällt. Der Niederschlag wird mit conc. Salpetersäure behandelt. Rhodanid wird hierbei zu Sulfat oxydiert, während Cyanid entweicht. Der Silberchloridniederschlag wird mit gelöstem Nickeltetracyanid umgesetzt und das in Freiheit gesetzte Nickel mit ÄTDE titriert. Zum Filtrat vom Chloridniederschlag wird eine gemessene Menge Bariumchlorid zugesetzt und der Überschuss an Barium mit ÄDTE bestimmt. In einem zweiten Teil der Probe wird Cyanid bestimmt durch Zugabe einer gemessenen Menge Nickelsulfats und Rücktitration des überschüssigen Nickels mit ÄDTE. Die Methode is rasch und genau. Sehr kleine Mengen einer Komponente können in Gegenwart grosser Mengen der beiden anderen Ionen bestimmt werden.

Résumé—L'auteur décrit une méthode complexométrique de dosage de cyanure, thiocyanate et de chlorure en présence l'un de l'autre. Sur une portion d'échantillon, les trois ions sont précipités par addition de nitrate d'argent en excès. Les précipités sont portés à ébullition avec de l'acide nitrique concentré. Le chlorure d'argent n'est pas altéré par ce traitement, cependant que le cyanure et le thiocyanate d'argent sont décomposés. Ce dernier est oxydé en sulfate, le cyanure étant chassé. Le précipité de chlorure d'argent est dissous dans une solution de tétracyanonickelate de potassium et le nickel libéré est titré par l'EDTA; les teneurs en chlorure sont déterminées indirectement. La solution de sulfate, après oxydation du thiocyanate, est traitée par un volume connu d'une solution de chlorure de baryum et l'excès de baryum est titré par une solution d'EDTA de même molarité. La différence entre les volumes de solution de chlorure de baryum et d'EDTA multipliée par un facteur donne les teneurs en thiocyanate de l'échantillon.

Le cyanure est dosé sur une deuxième partie d'échantillon en ajoutant un volume connu, en excès, d'une solution de sulfate de nickel et en titrant l'excès de nickel non combiné au cyanure. La différence entre les volumes des solutions de nickel et d'EDTA multipliée par un facteur donne les teneurs en cyanure.

La méthode est rapide et précise. Elle permet de doser de très faibles quantités de l'un des anions en présence de grandes quantités des autres.

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5-AMINO-2-BENZIMIDAZOLETHIOL AS AN ANALYTICAL REAGENT—II*

SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM AND THE SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

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Summary—5-Amino-2-benzimidazolethiol has been found to be a highly sensitive reagent for the colorimetric determination of rhodium^{III}. The orange-yellow complex of rhodium^{III} with the reagent, developed by heating in the pH range 2–5, shows maximum absorption at 370 mμ; it is practicable to use wavelength 390 mμ, where the reagent absorption is negligible. The colour system obeys Beer's law from 0·5 to 4·0 ppm of rhodium^{III}, the optimum concentration range being 1·0–3·5 ppm where the percentage relative error per 1% absolute photometric error is 2·88. Sandell's spectrophotometric sensitivity of the reaction is 0·004 μg/cm^2. Most of the common ions and rare metal ions, including uranium^{VI}, are without effect on the complex. Palladium^{II} interferes, producing a colour, but a simultaneous colorimetric method for determining rhodium^{III} and palladium^{II} in a mixture has been developed by determining rhodium and palladium together in hot solution and then subtracting the palladium determined in the cold. Interferences from ruthenium^{III} and larger amounts of iridium^{IV} are avoided by using EDTA (disodium salt) as a masking agent. The continuous variation and the molar ratio methods, applied at pH 3·42, indicate that rhodium^{III} forms with the reagent both 1:2 and 1:3 complexes, their dissociation constants being $2{\cdot}7 \times 10^{-12}$ and 6×10^{-17}, respectively.

INTRODUCTION

IN a previous communication,[1] the author introduced 5-amino-2-benzimidazolethiol as a very sensitive reagent for the colorimetric determination of micro amounts of palladium^{II}. It was shown that palladium can be determined at 390 mμ after developing the colour in the cold at pH 3·42 for 35 min. Rhodium^{III} gives no colour with the reagent in the cold, but when heated on a steam bath it develops an intense orange-yellow colour suitable for its spectrophotometric determination.

Until recently only the stannous chloride method for the colorimetric determination of rhodium has been widely studied by various workers but this method suffers from the drawback that almost all other platinum metals, present even in traces, will seriously interfere, hence their removal is absolutely necessary.[2] Recently thiomalic acid was introduced as a colorimetric reagent for rhodium,[3] but its sensitivity is lower than that of the stannous chloride method[4] or that of the present method developed by the author. Moreover, the tolerance limits of various ions, including the platinum metals, towards thiomalic acid seem to be very low.[3,5] There is therefore a need to search for new colorimetric reagents for rhodium which will not only be very sensitive but will also be relatively free from the interference of diverse ions including the platinum metals.

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The author after a critical study of the colour reaction of 5-amino-2-benzimidazolethiol with rhodium^{III}, finds that the reagent is ideally suited for the colorimetric determination of micro amounts of the metal.

EXPERIMENTAL

Apparatus

A Beckman DK1 automatic recording spectrophotometer was used for determining the wavelength-transmittance curves, and the absorbances of other solutions were obtained with a Beckman DU Spectrophotometer. In all cases, 1·00-cm silica cells were used.

A Beckman model G pH meter was employed for the pH determinations.

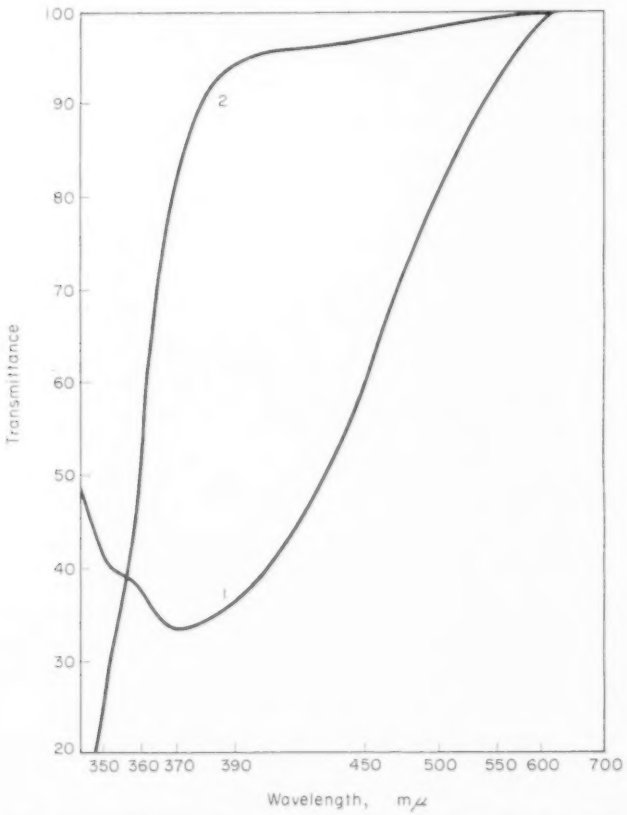

FIG. 1.—Wavelength-transmittance curves of 5-amino-2-benzimidazolethiol and its rhodium^{III} complex at pH 3·42.
Curve 1: 1·9 ppm of rhodium^{III} + 10 ml of 0·5% reagent.
Curve 2: 10 ml of 0·5% reagent diluted to 25 ml with buffer of pH 3·42.

Reagents

Standard rhodium solution: A rhodium^{III} stock solution was prepared from sodium rhodium chloride (Na_3RhCl_6) by dissolving it in dilute hydrochloric acid containing 10 ml of conc. HCl/litre. This solution was standardised by the 2-thiobarbituric acid method of Beamish *et al.*[6]

Other reagents: Solutions of reagent, buffer and other platinum metals and common ions were prepared in the manner described previously.[1,7]

Recommended procedure

Ten ml of 0·5% reagent solution were added to 1 ml of rhodium^{III} solution (12·5 to 100 μg of Rh) taken in a 25-ml beaker, and the mixture was heated on a steam bath for 25 min for complete colour development, and then cooled to room temperature. The orange-yellow coloured solution was transferred to a 25-ml volumetric flask, and the volume was made up with sodium acetate-acetic acid buffer of pH 3·42. The absorbance was then measured against a reagent blank prepared identically without rhodium.

DISCUSSION

Spectral curves

It is evident from the wavelength-transmittance curve of the complex (Fig. 1) that the maximum absorption (*i.e.* minimum transmittance) takes place at 370 mμ. But as the reagent absorption is also high in this region (*cf.* Fig. 1), a practical wavelength of 390 mμ was chosen for all subsequent measurements, the reagent absorption at this wavelength being negligible.

Effects of pH, reagent concentration and time

The complex is free from change of absorbance in the pH range 2–5. At higher pH values, however, there is a slight increase in the absorbance.

For 2–4 ppm of rhodium^{III}, 10 ml of 0.5% reagent are necessary for full colour development.

The colour does not develop at room temperature, but if heated on the steam bath for 20 min the full colour develops, and the absorbance value does not alter even after a longer heating period. Once formed, the complex maintains a constant absorbance for 24 hr.

Beer's law, optimum range and accuracy

The complex obeys Beer's law in the range 0·5–4·0 ppm of rhodium^{III} (*cf.* Fig. 2). The optimum concentration range, as obtained from Ringbom's[8] curve (Fig. 3), is between 1 and 3·5 ppm, where the percentage relative error per 1% absolute photometric error, evaluated by Ayres method,[9] is 2·88.

Sensitivity and molecular absorptivity

Sandell's spectrophotometric sensitivity,[4] as calculated from Beer's law data, is 0·004 μg/cm^2. The molecular absorptivity for the 1:3 complex is $1{\cdot}5 \times 10^5$.

Reproducibility

Ten samples of rhodium^{III} solution were taken for an examination of the reproducibility of the colour. The first five sets contained 2 ppm of rhodium^{III} in each case and absorbance values for these were found to be 0·475, 0·475, 0·470, 0·475 and 0·473. The second five sets contained 4 ppm of rhodium^{III} in each case and absorbance values were 0·93, 0·93, 0·93, 0·92 and 0·93. These results confirm the reproducibility of the method.

Effect of diverse ions

The effect of various ions on the colour system was investigated by adding different

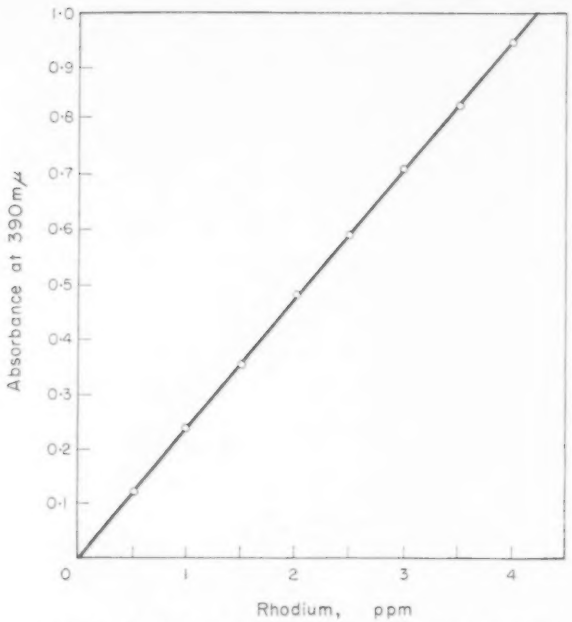

FIG. 2.—Beer's law plot for the rhodium^{III} complex at pH 3·42.

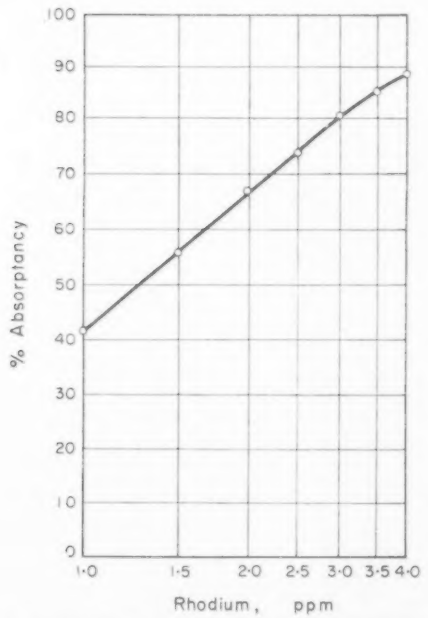

FIG. 3.—Calibration curve for the rhodium^{III} complex at 390 mμ; pH 3·42.

amounts of the ionic species to the rhodium^{III} solution and then developing the colour as outlined under recommended procedure. An increase or decrease of 0·005 unit in the absorbance value was taken to be an interference. It was observed that disodium

salt of ethylenediaminetetra-acetic acid (EDTA) could appreciably increase the tolerance limits for various ions. The results are given in Table I.

TABLE I.–DETERMINATION OF RHODIUM^{III} IN PRESENCE OF DIVERSE IONS
Rhodium taken, 4 ppm in each case

Ions	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*	Ions	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*
Ru^{3+}	32	4	Cd^{2+}	—	40
Ir^{4+}	—	4	As^{3+}	—	40
Ir^{4+}	32	8	Pb^{2+}	—	40
Au^{3+}	—	8	Mn^{2+}	—	20
Cu^{2+}	32	8	UO_2^{2+}	—	>70
Ni^{2+}	32	16	MoO_4^{2-}	—	40
Co^{2+}	—	32	WO_4^{2-}	—	40
Zn^{2+}	—	16	Cl^-	—	>300
Zn^{2+}	32	32	NO_3^-	—	>300
			SO_4^{2-}	—	>300

Platinum^{IV} should be absent, and osmium should be separated by distillation[4] of the volatile osmic acid (OsO_4).

Simultaneous determination of rhodium and palladium

Simultaneous determination of rhodium^{III} and palladium^{II} from a mixture is possible by taking advantage of the fact that palladium^{II}, when treated with the reagent at room temperature, develops its full colour intensity which does not change even after heating at 100°, whereas rhodium^{III} gives a colour with the reagent only after heating. Experiments also showed that the absorbance values of rhodium and palladium complexes at 390 mμ are quantitatively additive in character.

Procedure

An aliquot of the synthetic mixture of rhodium^{III} and palladium^{II} solutions was treated as described earlier for the determination of rhodium. The absorbance was measured at 390 mμ against a reagent blank to obtain the total amount of rhodium and palladium. To another aliquot of the same mixture of rhodium^{III} and palladium^{II} taken in a 25-ml volumetric flask, 10 ml of 0·5% reagent solution were added and the volume was made up with the buffer solution of pH 3·42. After allowing to stand for 35 min at room temperature, the absorbance was measured against a reagent blank at 390 mμ to ascertain the amount of palladium present. The absorbance value for palladium was then deducted from the total absorbance value for rhodium and palladium and the amount of rhodium was determined from this with reference to a standard curve.

The results as given in Table II show that rhodium and palladium can be determined from a mixture when they are present in a 1:1 or a 1:2 ratio. The latter figure represents the limit of applicability of the determination.

Composition of the complex in solution

The composition of the complex in solution was studied by the continuous variation[10] and molar ratio[11] methods.

For these studies, equimolecular solutions of rhodium^{III} and the reagent were mixed in the correct proportions in 25-ml beakers, and after heating on a steam bath for 25 min and subsequent cooling to

TABLE II.—SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

Rhodium^{III} taken, *ppm*	Palladium^{II} taken, *ppm*	Rhodium^{III} found, *ppm*	Palladium^{II} found, *ppm*
4·0	4·0	4·0	4·0
4·0	4·0	3·9	4·1
4·0	4·0	3·95	4·05
2·0	4·0	2·0	4·0
2·0	4·0	1·98	4·02
2·0	4·0	2·0	4·0

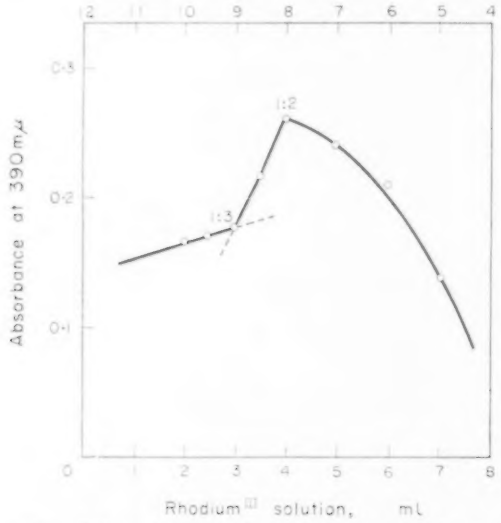

FIG. 4.—Determination of the ratio of rhodium^{III} to reagent by the continuous variation method.
Concn. of rhodium^{III} = concn. of reagent = $5{\cdot}69 \times 10^{-4}M$.
Total volume in each case = 12 ml; pH 3·42.

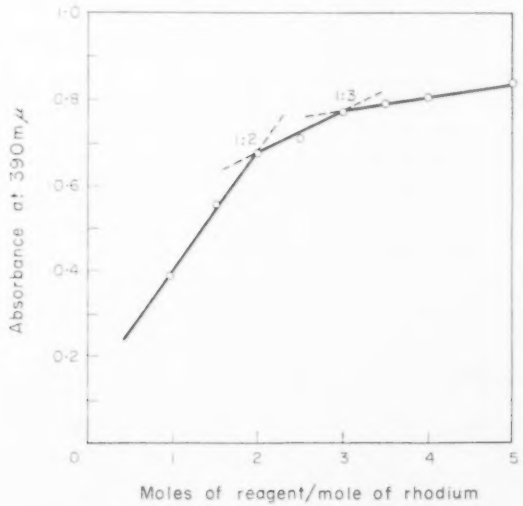

FIG. 5.—Determination of the ratio of rhodium^{III} to reagent by the molar ratio method.
Rhodium^{III} concn. = $9{\cdot}1 \times 10^{-5}M$ (constant); reagent concn. varied.

room temperature, the volume was made up to 25 ml in volumetric flasks by the buffer of pH 3·42. The absorbances were measured at 390 mμ against a water blank.

The results, as represented in Figs. 4 and 5, indicate that under the conditions employed rhodium^{III} forms both 1:2 and 1:3 complexes with the reagent. It appears from Fig. 5 that first the 1:2 complex is formed, and this quickly changes to the 1:3 complex when excess of the reagent is present.

Dissociation constants

By employing the absorption values of Fig. 5, the dissociation constants of both the 1:2 and 1:3 complexes were calculated from the equations $K = (\alpha C)(n\alpha C)^n / C(1 - \alpha)$ and $\alpha = (E_m - E_s)/E_m$ of Harvey and Manning.[12] The values were found to be $2{\cdot}7 \times 10^{-12}$ for the former complex and 6×10^{-17} for the latter.

Acknowledgements—The author expresses his indebtedness to Dr. Philip W. West, Boyd Professor of Chemistry, for providing laboratory facilities. He is also grateful to the Public Health Service of U.S.A. for financial support and to the authorities of Jadavpur University, Calcutta, India, for the kind sanction of study leave.

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Zusammenfassung—5-Amino-2-benzimidazolthiol wurde als hochselektives Reagens für die kolorimetrische Bestimmung von Rhodium(III) gefunden. Ein orangegelber Komplex entwickelt sich beim Erhitzen im pH-Bereich 2–5; das Absorptionsmaximum liegt bei 370 mμ; man kann auch bei 350 mμ arbeiten, wo die Absorptions des Reagenses vernachlässigbar ist. Beer's Gesetz wird zwischen 0.5 und 4.0 p.p.m. Rh erfüllt. Der optimale Konzentrationsbereich ist 1·0–3·5 ppm, wo der perzentuelle Fehler pro 1% absolutem photometrischem Fehler 2·88 beträgt. Sandell's spectrophotometrische Empfindlichkeit der Reaction ist 0·004 μg/cm². Die meisten gewöhnlichen Ionen, sowie seltenen Metallionen, einschliesslich U (VI) sind ohne Einfluss. Pd(II) stört durch Färbung; es ist aber möglich Pd + Rh in heisser Lösung und Rh in kalter Lösung zu bestimmen und so beide Metall zu ermitteln. Störungen durch Ru(III) und grossen Mengen Ir(IV) werden durch Maskieren mit ADTE ausgeschaltet. Bei pH 3·42 enstehen 1:2 und 1:3 Komplexe deren Dissoziationskonstanten zu $2{\cdot}7 \times 10^{-12}$ und 6×10^{-17} bestimmt wurden.

Résumé—L'auteur a trouvé que le 5-amino-2-benzimidazolethiol était un réactif très sensible pour le dosage colorimétrique du rhodium(III). Le complexe jaune orangé rhodium(III)-réactif, formé en chauffant dans le domaine de pH 2–5, présente un maximum d'absorption à 370 mμ; il est pratique d'utiliser une longueur d'onde de 390 mμ, pour laquelle l'absorption du réactif est négligeable. Le système coloré suit la loi de Beer de 0,5 à 4,0 p.p.m. de rhodium(III), le domaine de concentration le meilleur étant 1,0 à 3,5 p.p.m. dans ce domaine le pourcentage d'erreur relative, pour une erreur photométrique absolue de 1%, est 2,88. La sensibilité spectrophotométrique de Sandell de la réaction est 0,004 μg/cm². La plupart des ions communs et des ions métalliques rares, l'uranium(VI) y compris, n'ont aucune influence sur le complexe. Le palladium(III) gêne en donnant une couleur, mais l'auteur a mis au point une méthode colorimétrique de dosage simultané de rhodium(III) et palladium(II) dans un mélange: le rhodium et le palladium sont déterminés ensemble dans la solution chaude, puis le palladium déterminé à froid est soutsrait. Les interférences du ruthénium(III) et de grandes quantités d'iridium(IV) sont évitées en complexant ces métaux par l'E.D.T.A. (sel disodique). Les méthodes de variation continue et du rapport molaire, appliquées à pH 3,42, indiquent que le rhodium(III) forme avec le réactif les complexes 1/2 et 1/3; leurs constantes de dissociation sont respectivement $2{,}7 \cdot 10^{-12}$ et $6 \cdot 10^{-17}$.

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THE DETERMINATION OF TRACES OF GOLD IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method has been developed to determine very small concentrations of gold in samples of platinum. The Harwell nuclear reactor DIDO has been used as the source of neutrons. Following irradiation, gold has been separated radiochemically from samples and standards. ^{198}Au activity has been assayed by a discriminated γ-counting method in which ^{199}Au activity produced from activation of platinum is not recorded. Results are quoted for the gold contents of some pure platinum samples.

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OWING to limitations of conventional methods of analysis, radioactivation procedures have been developed to determine very small quantities of impurities in samples of platinum.[1–3] In this paper the determination of traces of gold in platinum by neutron-activation is reported. The nuclear reactor DIDO at Harwell has been used as the source of neutrons and a comparative method of analysis has been employed. To avoid neutron self-screening differences between samples and standards,[4] standards have been prepared by the admixture of small known quantities of gold with analytical samples.

Gold has only one stable isotope, ^{197}Au. On irradiation with neutrons of thermal energies this yields the radionuclide ^{198}Au by a nuclear reaction of the (n,γ) type. The ^{198}Au may undergo a further (n,γ) reaction giving ^{199}Au. Activation cross-sections,[5] σ, for the reactions are

$$^{197}\text{Au}(\text{n},\gamma)^{198}\text{Au} \qquad \sigma = 96 \text{ barns}$$

$$^{198}\text{Au}(\text{n},\gamma)^{199}\text{Au} \qquad \sigma = 26{,}000 \text{ barns}$$

and nuclear data[6] for the radionuclides ^{198}Au and ^{199}Au are given in Table I.

TABLE I. PROPERTIES OF THE RADIONUCLIDES GOLD-198 AND GOLD-199

Nuclide	Half-life, *days*	Decay modes, radiations and energies (*MeV*)	Decay product
^{198}Au	2·697	β^- 0·960 (~100%), (others) γ 0·411 (96·4%), 0·675, 1·087,	^{198}Hg (stable)
^{199}Au	3·14	β^- 0·460 (6·4%), 0·302 (69·3%), 0·251 (24·3%) γ 0·0497, 0·1583, 0·2080	^{199}Hg (stable)

The neutron-activation analysis of traces of gold in platinum is made difficult by the fact that ^{199}Au is produced in considerable yield from platinum by the sequence

$$^{198}\text{Pt}(\text{n},\gamma)^{199}\text{Pt} \xrightarrow[t_{1/2} = 31 \text{ min}]{\beta^-} {}^{199}\text{Au}.$$

The problem arises, therefore, of assaying small amounts of ^{198}Au in the presence of a preponderance of ^{199}Au. Because ^{198}Au and ^{199}Au have such similar half-lives it is impossible to resolve the activities satisfactorily from decay measurements. However, the differences in the energies of the γ-rays emitted by the two radionuclides do enable the ^{198}Au to be measured.

^{198}Au may be produced from platinum by the sequence

$$^{196}Pt(n,\gamma)^{197}Pt \xrightarrow[t_{1/2}=18\ hr]{\beta^-} {}^{197}Au(n,\gamma)^{198}Au$$

but calculation[7] shows that under the conditions employed in the present work this would give rise to a spurious gold content of platinum samples corresponding to only *ca.* 10^{-4} ppm.

EXPERIMENTAL

Irradiation

The samples of platinum for analysis were in the form of powdered metal sponge. Weighed quantities of 0·1 g were sealed in silica tubes of internal diameter 4 mm. Standards were prepared by adding weighed portions (*ca.* 0·02–0·04 g) of a standard solution of gold (100 mg of Au/litre) to 0·1-g samples of platinum in silica tubes. The liquid was allowed to soak into the metal powder, then was carefully evaporated to dryness, after which the tubes were sealed.

Standards containing the added gold and samples to which no gold had been added were packed together with silica wool in standard aluminium cans, 3 in. long and 1 in. diameter, and were sent to Harwell for neutron activation. Irradiation was for 2·5 hr in the Pile DIDO with a thermal neutron flux of 8×10^{11} n/cm²/sec.

Following delivery from Harwell after irradiation, the samples and standards were analysed radiochemically for ^{198}Au.

Radiochemical separation

The chemical procedure for the separation of gold involved the use of carrier chemistry, solvent extraction and precipitation.

After dissolution of the samples and standards in *aqua regia*, together with gold carrier, the gold was separated from most other elements by extraction into ether.[8] Further purification was achieved by precipitation of gold metal by means of reduction with hydroquinone. The last traces of contaminating elements were removed by extraction of gold^{III} from hydrochloric acid solution into ethyl acetate. The gold^{III} was finally converted by hydroquinone reduction to the metallic state in which form it was counted.

Rather similar separation procedures have been employed by other workers in radioactivation analyses of gold in geological,[9,10] cosmological,[4] and biological[11,12] materials and in refined silver and nickel cathodes.[13]

Details of the radiochemical separation used in the present work are as follows:

Step 1. Open the silica irradiation tubes and transfer the activated samples and standards to clean 50-ml glass centrifuge tubes. To each add 1 ml of Au carrier (10 mg of Au/ml as Au^{III} in 0·1*M* HCl) and 2 ml of 12*M* HCl. Wash out the irradiation tubes thoroughly with hot 6*M* HCl and transfer the washings to the centrifuge tubes. Add 1 ml of 16*M* HNO_3 and slowly dissolve each sample of platinum by heating on a water bath. Boil for *ca.* 10 min and during this period add two 1-ml portions of 12*M* HCl.

Step 2. Adjust the strength of the solution to *ca.* 1*M* in HCl and cool. Agitate the solution with three successive 10-ml portions of diethyl ether. Separate and combine the organic layers. Wash the combined extract twice with 10-ml portions of 2*M* HCl saturated with ether and reject the washings. Separate the organic phase into a clean 50-ml centrifuge tube and warm on a water bath until the ether has completely evaporated.

Step 3. Dilute the residue with 20 ml of hot H_2O and heat to boiling. Add 2 ml of a freshly prepared 5% aqueous solution of hydroquinone and digest for several min. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate of gold in 1 ml of *aqua* regia, add 1 ml of 12*M* HCl, and dilute to 20 ml with H_2O. Extract with two successive 10-ml portions of ethyl acetate. Combine the organic layers in a clean 50-ml centrifuge tube, wash twice with 10 ml of 2*M* HCl and reject the washings. Evaporate off the ethyl acetate and to the residue add 25 ml of hot 1*M* HCl.

Step 5. Heat on a water bath and add 2 ml of 5% hydroquinone solution. Digest for 10 min, centrifuge and discard the supernate. Wash the precipitate of gold twice with 10 ml of hot H_2O and once with ethanol. Transfer the metal powder as a slurry in ethanol with a pipette onto a weighed aluminium counting tray (A.E.R.E. Cat. No. 4–3/1068). Dry under a heater-lamp and weigh to establish the chemical yield (usually *ca.* 75%).

Counting of the final gold precipitates

The final precipitates of gold from samples and standards were counted through an Al-Pb sandwich absorber (852 mg/cm² Al, 1·80 g/cm² Pb, 98 mg/cm² Al) with a 1·5-in. diam. × 1 in. NaI(Tl) crystal scintillation counter. A discriminator bias voltage was applied to the output of the counter to cut out the γ-rays of ^{199}Au. The observed counting rates were corrected for background and chemical yield and for any decay of significance between counting samples and standards.

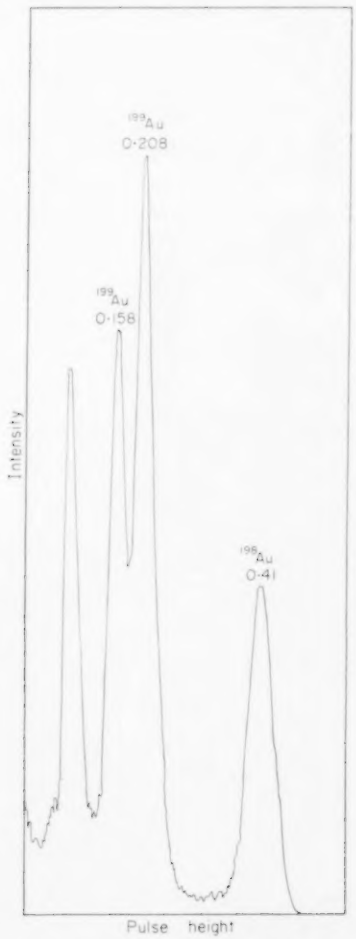

FIG. 1.—γ-Ray spectrum of gold radiochemically separated from neutron-irradiated platinum. (Energies in MeV).

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The spectrum obtained from a final gold precipitate measured through an Al-Pb sandwich absorber with a NaI(Tl) crystal γ-ray spectrometer is shown in Fig. 1. It can be seen from this that by application of sufficient bias voltage γ-rays of ^{198}Au may be counted with no interference from ^{199}Au.

An additional check that only ^{198}Au activity from the final precipitates was being counted was obtained from decay measurements. Decay curves were straight lines corresponding well with published values[6] for the half-life of ^{198}Au (Fig. 2).

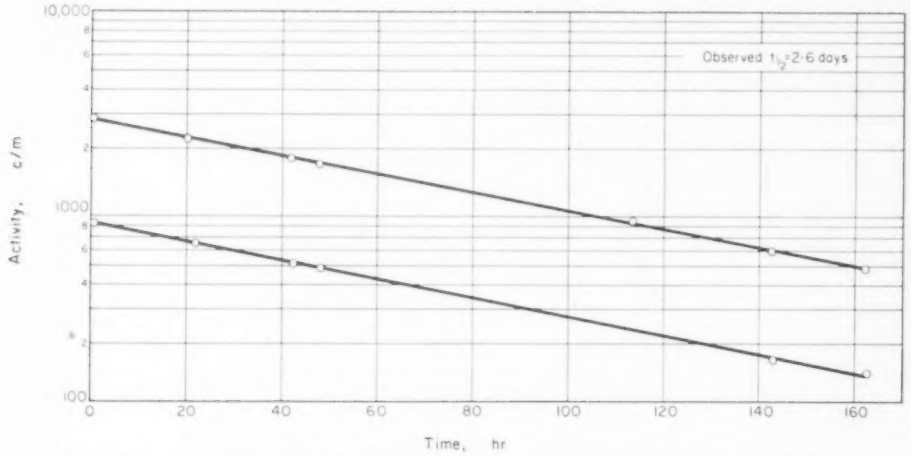

Fig. 2.—Decay curves of final gold precipitates measured by discriminated γ-scintillation counting.

RESULTS AND DISCUSSION

In Table II are shown results of neutron-activation analyses of pure samples of platinum.

Table II. Gold contents of samples of platinum determined by neutron-activation analysis

Sample	Gold content, *ppm*
Pt 1	0·61, 0·69, 0·69
Pt 2	3·4, 3·6
Pt 3	0·70, 0·78, 0·83, 0·74
Pt 4	0·86, 0·81
Pt 5	2·5, 2·7
Pt 6	1·0, 1·0
Pt 7	1·1, 1·1, 1·1

Neutron-activation normally provides an exceptional sensitivity for the analysis of gold, *e.g.* Gibbons[12] has reported that as little as 10^{-10} g of the element can be determined in biological materials. In the special case of platinum samples, nuclear considerations prevent full realisation of the potential sensitivity; nevertheless, 0·1 ppm of gold* may be determined by the method described in the present work, and this level appears to cover industrial requirements.

* This content of gold would give *ca.* 50 cpm above the background count.

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Zusammenfassung—Neutronenaktivierung wurde zu Bestimmung sehr kleiner Mengen von Gold in Platinmetal angewendet. Der Harwellreaktor DIDO wurde als Strahlenquelle eingesetzt. Nach der Bestrahlung wurde Gold mittels radiochemischer Methoden aus Probe und Standard isoliert und die Aktivität des ^{199}Au selektiv gezählt. Resultate für einige Platinproben werden mitgeteilt.

Résumé—Les auteurs ont mis au point une méthode pour doser de très faibles concentrations d'or dans des échantillons de platine par activation neutronique. Le réacteur nucléaire DIDO de HARWELL a été utilisé comme source de neutrons. Après l'irradiation, l'or a été séparé radiochimiquement des échantillons et des étalons. L'activité de ^{198}Au a été déterminée par une méthode de comptage des rayons gamma dans laquelle l'activité de ^{199}Au produit par l'activation du platine n'est pas enregistrée. Les résultats sont donnés en teneurs en or des échantillons de platine pur.

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SIMULTANEOUS INFRARED DETERMINATION OF SULPHATE, NITRATE AND NITRITE IN WATER SAMPLES

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Summary—Small quantities of nitrate, nitrite and sulphate ions may be determined simultaneously by infrared spectrophotometry, utilising the potassium bromide disk technique. The solid samples are prepared by freeze-drying aqueous solutions of these ions containing potassium bromide. An anion-exchange procedure is readily coupled with the infrared measurement through the freeze-drying step. This permits the concentration of very dilute sample solutions, and eliminates the interferences of phosphate, carbonate, and organic matter. The method has been applied to the determination of nitrate, nitrite and sulphate in water samples, where it is found to compare favourably with other methods.

ALTHOUGH infrared spectrophotometry has become a routine tool for the solution of countless analytical problems, there have been few applications to the determination of inorganic ions. The catalogue of Miller and Wilkins[3] showed that many inorganic ions exhibit potentially useful infrared absorption bands. Studies in this laboratory demonstrated that small quantities of sulphate could be determined by infrared spectrophotometry, and that freeze-drying coupled with the potassium bromide disk technique, permitted the ready adaptation of infrared measurements to samples presented as aqueous solutions.[2,5] Furthermore, these techniques can be combined easily with preliminary chromatographic and ion-exchange separations.

In a detailed study of the infrared measurement of sulphate, nitrate, and nitrite ions in a potassium bromide matrix,[4] it was found that small quantities of these three ions could be readily determined, singly or in admixture with an accuracy adequate for many purposes. The most serious interfering substances likely to be encountered in practical work were found to be phosphate, carbonate, and organic matter. This paper describes a simple ion-exchange separation that eliminates these interferences and permits the simultaneous infrared determination of sulphate, nitrate and nitrite in realistic analytical situations. To demonstrate the utility of the method, its application to the analysis of water samples is described.

EXPERIMENTAL

Apparatus and reagents

Infrared spectra were recorded with a Perkin-Elmer Model 137 "Infracord" spectrophotometer. Disks were prepared with a Hilger H920 die obtained from Jarrell-Ash Co., Newtonville, Mass., using a Loomis 20-ton hydraulic press. Solutions were freeze-dried in lipless test-tubes about 10 cm long, using a 24-port VirTis freeze-dryer.

The anion-exchange column was a conventional one, about 10 × 1 cm, packed with Dowex 1-X8, 100–200 mesh. After ordinary washing with dilute reagent solutions, the resin continued to bleed sufficient organic matter to interfere seriously with the infrared measurements. This difficulty was eliminated by washing the column with 10*M* nitric acid, after which it was converted to the bromide form for use in the analytical procedure.

A special grade of potassium bromide suitable for infrared work, manufactured by E. Merck, Darmstadt, Germany, was obtained from Terra Chemicals Inc., New York, N.Y. All other chemicals were of the usual reagent grade.

Preliminary experiments

According to Wheaton and Bauman,[6] who studied the selectivity of Dowex 1 in the chloride form for a number of univalent anions, nitrite, nitrate and bisulphate are retained much more strongly on the resin than are bicarbonate and dihydrogenphosphate. Because the column in the present work was in the bromide form and because pH values were not such as to give exclusively univalent ions, it was necessary to establish experimentally column operating conditions that would ensure a clean separation of phosphate and carbonate from nitrate, nitrite and sulphate. In a series of preliminary experiments, the elution behaviour of the five anions was studied with potassium bromide solutions ranging from 0·01 to 1*M*, using spot tests to estimate concentrations in the eluate. In all cases, the order of elution was: phosphate, carbonate, sulphate, nitrite, nitrate. Later quantitative infrared measurements of freeze-dried eluates confirmed this order.

The following procedure was established as a result of these studies: after a mixture of the five anions has been placed on a 10-cm column, phosphate and carbonate are eluted with 0·05*M* potassium bromide solution, then sulphate, nitrite, and nitrate are eluted with 1*M* potassium bromide. About 7 column volumes of the 0·05*M* eluant solution remove phosphate and carbonate completely, whereas the desired anions do not break through until 9 or 10 column volumes have passed. The latter are then eluted very rapidly by increasing the eluant concentration to 1*M*. Fig. 1 shows the elution of the anions under these conditions. Organic matter, in the quantities encountered in typical water samples, is reduced below the interference level during the ion-exchange procedure.

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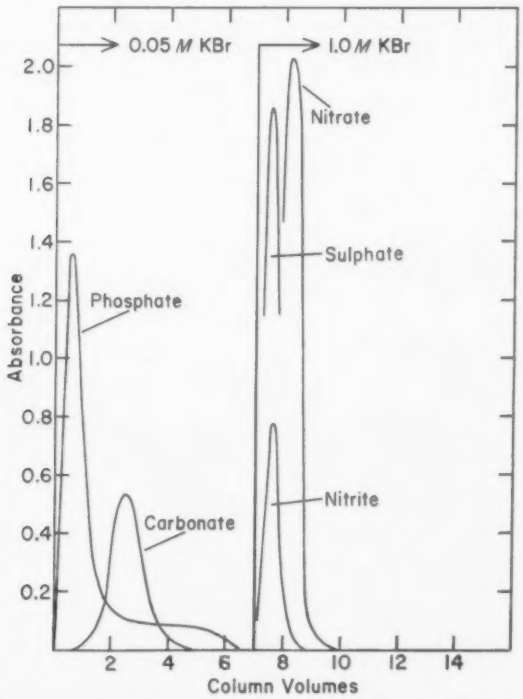

FIG. 1.—Elution curves for phosphate, carbonate, sulphate, nitrite and nitrate from Dowex 1 column under conditions of procedure given in text.

Fig. 2 shows the infrared spectrum of a typical freeze-dried column eluate containing nitrate, nitrite and sulphate. As is nearly always the case with infrared absorption bands, it is difficult here to decide exactly how to establish the base-lines from which to measure I and I_0 values for absorbance calculations. In the present work, the best reproducibility was obtained using base-lines connecting points at fixed distances on either side of the minimum. For example, with the nitrate band (7·23 μ, 1383 cm^{-1}), the baseline was drawn between transmittances at 7·1 and 7·5 μ. With the nitrite band

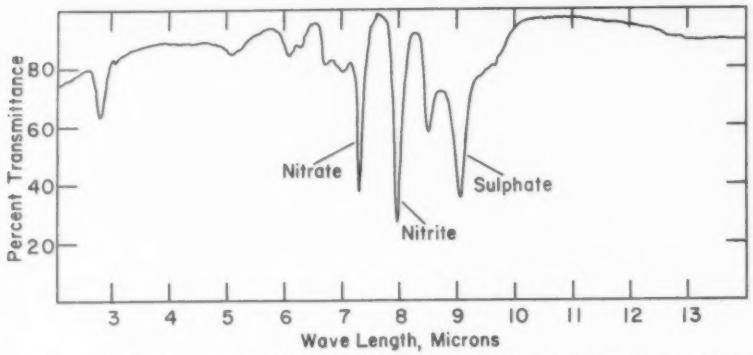

FIG. 2.—Infrared spectrum of freeze-dried column eluate containing nitrate, nitrite and sulphate.

(7·87 μ, 1271 cm^{-1}), distances of 0·2 μ on either side were again used, while with the sulphate band (9·00 μ, 1111 cm^{-1}), the distances were 0·3 μ. It is recognised that other workers may have different preferences regarding base-lines

Fig. 3 shows calibration curves for nitrate, nitrite and sulphate. The curves are seen to be linear over the absorbance range where one would normally work. With standard solutions of these ions, the same curves are obtained whether or not the ion-exchange step is included, showing that quantitative recovery from the column is obtained. The calibration curves are reasonably reproducible but, of course, it is good practice to run standards through the procedure along with the unknown samples.

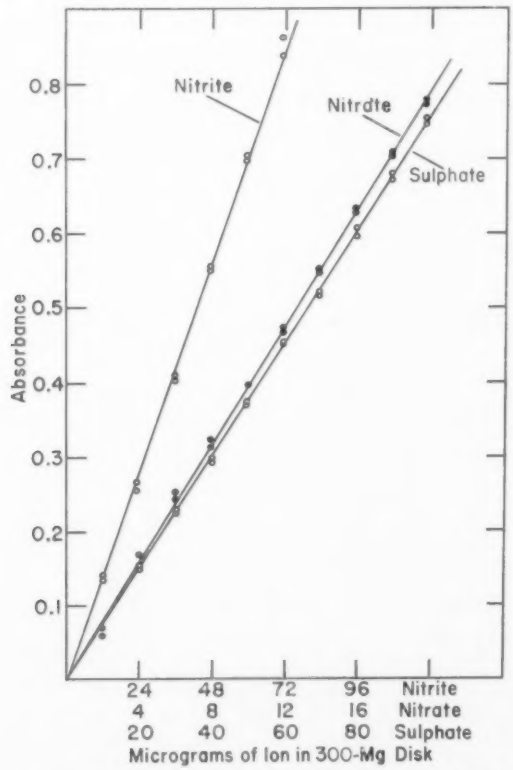

FIG. 3.—Calibration curves for nitrate, nitrite and sulphate.

Procedure

A new anion-exchange column should be washed with several column volumes of strong nitric acid; about 50 ml of 10*M* acid was used in this work. Then rinse the column with distilled water, convert it into the bromide form by treatment with several column volumes of 4*M* potassium bromide, and finally wash it with distilled water. The column is now ready to receive the sample. Such a column may, of course, be used repeatedly.

The volume of water sample passed through the column may be varied widely depending upon its composition, the extent to which the eluate is diluted, and the quantity of eluate taken for freeze-drying. One often knows from experience the approximate concentrations in the sample, and can adjust the conditions accordingly. With typical fresh-water samples, a volume of 500 ml was passed through the column in the present work. A flow rate of 5 ml per min. was satisfactory. On the other hand, a 50-ml sample of sea-water was sufficient.

Wash the column with about 30 ml of distilled water. Elute phosphate and carbonate using about 70 ml of 0·05*M* potassium bromide solution. In the present work, this eluate was discarded. Then elute sulphate, nitrate and nitrite with about 40 ml of 1*M* potassium bromide solution. It is important to know how much of this potassium bromide solution is used, and to recover practically all of it from the column, because this potassium bromide appears in the disk finally taken for infrared measurement and determines what we may call a dilution of the sample. Thus, it is well to rinse the column with a little distilled water after the 1*M* potassium bromide has passed, and to add these washings to the eluate solution. Any 0·05*M* potassium bromide remaining in the column prior to this final elution, on the other hand, contributes negligibly to the total quantity of potassium bromide ultimately obtained.

Dilute the column eluate to some known volume. In the present work, 50 ml was generally convenient for fresh-water samples. Place an aliquot of this solution (1 ml was usually used here) in a freeze-drying tube, and add potassium bromide, either as weighed solid or as a standard solution, to bring the total quantity of potassium bromide in the tube to the weight desired for a disk. The authors prefer 300-mg disks but other weights are permissible. After mixing the solution thoroughly, dip the tube into a freezing mixture of dry ice and acetone with a swirling motion so that the liquid freezes rapidly in a thin layer extending part way up the wall of the tube. Keep the sample in the freezing mixture until it is to be evacuated, then freeze-dry it overnight. Once the freeze-drying begins, the sample remains frozen without further external cooling, and the process requires no attention.

Transfer the freeze-dried material from the tube to the die, form it into an even layer, and press the disk. The authors evacuated the die for about 1 min, then pressed the disk with a total applied force of about 20,000 lb for 5 min. This force corresponds to a pressure of a little over 100,000 lb per sq. in. with the die used in this work. Remove the disk from the die and record its spectrum from about 6 to 11 μ, using a pure potassium bromide disk of the same weight in the reference beam. Draw the base-lines on the chart, measure I and I_0 values for the nitrate, nitrite and sulphate bands, and calculate their absorbance values. Weigh the disk, and correct the absorbance values for any of the material that may have been lost in transfer from the freeze-drying tube to the die. Compare these corrected absorbances with calibration curves obtained by running known quantities of nitrate, nitrite and sulphate through the procedure to obtain the quantities of these ions in the disk. Then, using appropriate dilution factors, calculate the quantities in the original sample.

Samples may sometimes be encountered in which the concentrations of the three anions are not appropriate for the simultaneous measurement. It may be, for example, that if a workable quantity of sulphate is obtained in the final disk, the nitrate absorbance will be too large for measurement with the desired accuracy. In such cases, it may be best to freeze-dry two aliquots, one larger than the other, in order to place both absorbance measurements in the desired range.

RESULTS

Synthetic solutions

To aliquots of a solution containing 40 ppm of sulphate, 48 ppm of nitrite and 8 ppm of nitrate, were added varying quantities of phosphate and carbonate. These solutions were run through the ion-exchange separation and infrared determination. It was found that the results were not affected by the presence of phosphate until the

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level of 800 ppm was reached, after which the column separation broke down and interfering phosphate bands appeared in the infrared spectrum. Presumably a column of sufficient length could achieve the separation of any desired quantity of phosphate, but the 10-cm column described here is certainly adequate for most water samples. Similar quantities of carbonate are likewise adequately separated.

The reproducibility of the method was studied with synthetic solutions containing nitrate, nitrite and sulphate. Within the absorbance range where errors are nearly minimal, say 0·2 to 0·8, the standard deviations for 20 samples were about 2% relative for each of the three ions.

Water samples

The method was tested on three water samples: tap water from the Dekalb County, Georgia, public water supply; a small creek in the Atlanta area; and a seawater sample taken from the Gulf of Mexico near Sarasota, Florida. For comparison purposes, the same samples were analysed by other methods as follows: sulphate by the barium chloranilate colorimetric method;[1] nitrite by the sulphanilic acid-alpha-naphthol colorimetric method;[7] and nitrate by reduction to nitrite with zinc followed by the above nitrite method.[7] The results are summarised in Table I. It may be seen that the only serious discrepancy occurs with nitrate, higher results being obtained with the infrared method. The colorimetric method, predicated as it is upon quantitative reduction of nitrate to nitrite, is suspect, in the authors' opinion. It is important

TABLE I. RESULTS OF ANALYSIS OF WATER SAMPLES

Sample	Ion	Infrared method, *ppm*	Other methods (see text), *ppm*	Difference between methods, %
Tap water	NO_3^-	0·36	0·32	11·1
	NO_2^-	0·00	0·00	—
	SO_4^{2-}	4·31	4·35	0·9
Creek water	NO_3^-	0·93	0·82	11·8
	NO_2^-	0·020	0·018	7·5
	SO_4^{2-}	4·79	4·69	2·1
Sea water	NO_3^-	0·96	0·91	5·7
	NO_2^-	36·8	35·8	2·7
	SO_4^{2-}	385	379	1·6

to note that the infrared method was much faster than the sum of the others for the three ions, provided we do not count the freeze-drying time. Since freeze-drying requires no attention except at start and finish, and since many samples can be freeze-dried together, it is reasonable to exclude it in determining operator time per sample.

Acknowledgement—This work was supported by the U.S. Atomic Energy Commission through Research Contract No. AT-(40-1)-2046.

Zusammenfassung—Kleine Mengen von Nitrat, Nitrit und Sulfat können mittels Infrarotspektrophotometrie gleichzeitig bestimmt werden. Die Proben werden durch Gefriertrocknung der Lösungen, die Kaliumbromid enthalten, zubereitet. Einsatz von Anionenaustauschern erlaubt Anreicherung der

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Ionen und gleichzeitige Abtrennung von störendem Phosphat, Carbonat und organischem Material. Die Methode wurd zur Bestimmung der Ionen in wasser herangezogen und die Resultate stimmten mit denen nach anderen Methode erhaltenen gut überein.

Résumé—De petites quantités d'ions nitrate, nitrite et sulfate peuvent être dosées simultanément par spectrophotométrie infra-rouge, en utilisant la technique du disque de bromure de potassium. Les échantillons solides sont préparés en désséchant par congélation les solutions aqueuses de ces ions contenant du bromure de potassium. Une méthode d'échange d'anions est facilement associée à la mesure infra-rouge après le stade de séchage par congélation. Cela permet d'utiliser des solutions d'échantillon très diluées et élimine l'interférence des ions phosphaté, carbonate et des matières organiques. La méthode a été appliquée au dosage de nitrate, nitrite et sulfate dans des échantillons d'eau; on peut la comparer favorablement aux autres méthodes.

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VOLUMETRISCHE BESTIMMUNG VON MAGNESIUM IN GEGENWART VON CALCIUM

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Zusammenfassung—Auf Grund der verschiedenen Stabilität der Magnesium-, Calcium-, und Barium-ÄDTE und -ÄGTE Komplexe, wird eine volumetrische Methode vorgeschlagen, die auf folgender Reaktion:

$$Mg^{+2} + Ca^{+2} + Ba\text{-ÄGTE} + SO_4^{-2} \rightarrow Ca\text{-ÄGTE} + BaSO_4 + Mg^{+2}$$

Die Methode erlaubt die Magnesiumbestimmung bei Gegenwart von Calcium bis zum Verhältnis 1:150. Die Ergebnisse werden durch den $BaSO_4$-Niederschlag nicht wesentlich beeinflusst.

DIE chelometrische Bestimmung von Calcium und Magnesium hat eine weite Anwendung in der Analyse verschiedener Materialien gefunden.[1] Bei den bisher vorgeschlagenen Methoden erhält man den Magnesiumgehalt entweder aus der Differenz nach Titration der Summe von Calcium und Magnesium (pH 10) mit Eriochromschwarz T als Indikator in einem Aliquot das Calcium nach der Ausfällung des Magnesium als Hydroxyd bei pH 12,5 oder mehr, oder durch Titration des Magnesium nach vorheriger Ausfällung des Calcium in einem zweiten Aliquot.

Vor kurzem haben Reilley und Mitarbeiter[2] und Ringbom mit Mitarbeitern[3] die Calciumbestimmung in Gegenwart von Magnesium durchgeführt, indem sie eine Lösung von ÄGTE (Äthylenglykol-bis-(β-aminoäthyläther)-N,N′-tetraessigsäure) als Masslösung anwandten. Wegen der geringen Stabilität des Mg-ÄGTE-Komplexes (log K = 5,21)[4] hat man jedoch diesem Chelon als Masslösung wenig Aufmerksamkeit geschenkt. Der Unterschied in der Stabilität des Calcium- und Magnesium-ÄGTE-Komplexes-von Reilley[2] und Ringbom[3] zur Calciumbestimmung benutzt- und die Tatsache, dass der Barium-ÄGT-Komplex ebenfalls stärker ist als der Magnesium-Komplexes (log $K_{Ba-ÄGTE} = 8{,}41$)(4), aber schwäeher als der Calcium-Komplex (log $K_{Ca-ÄGTE} = 10{,}97$), macht jedoch die Maskierung des Calcium bei der Titration des Magnesium mit ÄDTE möglich. Dazu verwendet man die folgende Reaktion:

$$Mg^{+2} + Ca^{+2} + Ba\text{-ÄGTE} + SO_4^{-2} \rightarrow Ca\text{-ÄGTE} + BaSO_4 + Mg^{+2}$$

Das Calcium verdrängt quantitativ das Barium aus seinem Komplex und das freigewordene Ba^{+2} fällt mit dem an-wesenden Sulfation aus. Im Gegensatz dazu ist das Magnesium nicht fähig, das Barium aus seinem Komplex zu verdrängen, weshalb man mit ÄDTE und Erichromschwarz T in ammoniakalischem Medium titrieren kann.

Die Methode erlaubt die Magnesiumbestimmung bei Gegenwart beliebiger

Calcium-Mengen, wobei die Trennung vom gefälltem $BaSO_4$ nicht nötig ist, weshalb das Verfahren viel rascher und genauer ist als irgendeines der bisher angewendeten.

EXPERIMENTELLER TEIL

Reagentien und Lösungen

0,05 m ÄDTE (zweisbasisches Salz)

0,05 m Ba-ÄGTE. In ca. 700 ml zweifachdestillierten Wassers werden 19,1000 gr ÄGTE (Chel DE, Geigy) und 9,8500 gr reinstes Bariumcarbonat verteilt. Man schüttelt bis zur völligen Lösung, filtriert und verdünnt auf 1 Liter.

1%ige Lösung von wasserfreiem Natriumsulfat.

0,2%ige Lösung von Methylrot

Eriochromschwarz T und NaCl im Verhältnis 1:200 gemischt.

Puffer pH 10, nach Schwarzenbach.

Verfahren

Zu 50 ml der fast neutralen Lösung fügt man einen leichten Überschuss der Ba-ÄGTE-Lösung hinzu, verdünnt mit Wasser, gibt die Pufferlösung und genügend Na_2SO_4-lösung zu, Sedass alles freigewordene Barium ausgefällt wird, und 2 Tropfen Methylrotlösung, sowie eine Messerspitze der Eriochromschwarz T-NaCl-Mischung. Anschliessend titriert man das Magnesium mit der 0,05 m ÄDTE-Masslösung bis zum Farbumschlag von Rot auf ein fast farbloses Grau.

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ERGEBNISSE

Wir haben eine Reihe von Bestimmung durchgeführt, in welchen eine gleichbleibende Menge von Magnesium (10 ml der 0,05 m Lösung) in Gegenwart wechselnder Calciummengen bestimmt wurde (von 4 ml einer 0,05 m Lösung bis 150 ml einer 0,5 m Lösung) in der Absicht, die Anwendbarkeit des Verfahrens bei im Verhältnis zu Magnesium viel grösseren Calciummengen zu überprüfen. In Tab. 1 (Abb. 1) sind die erhaltene Werte bis zum Verhältnis Mg:Ca 1:50 zusammengefasst.

Die Tabelle 2 (Abb. 2) zeigt die erhaltenen Ergebnisse bei einem Verhältnis Mg:Ca von 1:75 bis 1:150.

TABELLE I. BESTIMMUNG VON MAGNESIUM IN GEGENWART VON CALCIUM BEI EINEM VERHÄLTNIS Mg:Ca BIS ZU 1:50

Num.*	Mg^{+2} gegeben, *mg*	Ca^{+2} zugefügt, *mg*	Verhältnis Mg/Ca	0,05 m ÄDTE verbraucht, *ml*	Mg^{+2} gefunden *mg*	Unterschied, *mg*
1–1	12,16	8,02	1:0,4	9,96	12,11	−0,05
2–1	12,16	16,03	1:0,8	10,06	12,23	+0,07
3–1	12,16	24,05	1:1,2	9,96	12,11	−0,05
4–1	12,16	32,06	1:1,6	10,08	12,26	+0,10
5–1	12,16	40,08	1:2	10,08	12,26	+0,10
6–1	12,16	48,10	1:2,4	9,88	12,01	−0,15
7–1	12,16	56,11	1:2,8	10,16	12,36	+0,20
8–1	12,16	80,16	1:4	10,21	12,42	+0,26
9–1	12,16	150,30	1:7,5	10,11	12,29	+0,13
10–1	12,16	200,40	1:10	10,08	12,26	+0,10
11–1	12,16	501,00	1:25	10,15	12,34	+0,18
12–1	12,16	1.002,00	1:50	10,12	12,31	+0,15

* Die Werte sind die Mittel von 5 Bestimmungen

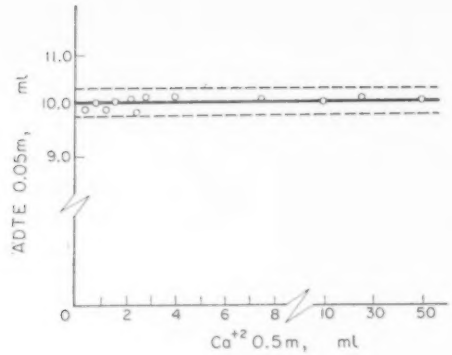

Abb. 1

TABELLE II. BESTIMMUNG VON MAGNESIUM IN GEGENWART VON CALCIUM BIE EINEM VERHÄLTNIS Mg:Ca VON 1:75 BIS 1:150

Num.*	Mg^{+2} gegeben *mg*	Ca^{+2} zugefügt, *g*	Verhältnis Mg:Ca	0,05 m ÄDTE verbraucht, *ml*	Mg^{+2} gefunden, *mg*	Unterschied, *mg*
1–2	12,16	1,503	1:75	10,14	12,33	+0,17
2–2	12,16	1,804	1:90	10,26	12,48	+0,32
3–2	12,16	2,204	1:110	9,97	12,12	−0,04
4–2	12,16	2,605	1:130	10,34	12,57	+0,41
5–2	12,16	3,006	1:150	10,16	12,36	+0,20

* Die Werte sind die Mittel von 5 Bestimmungen.

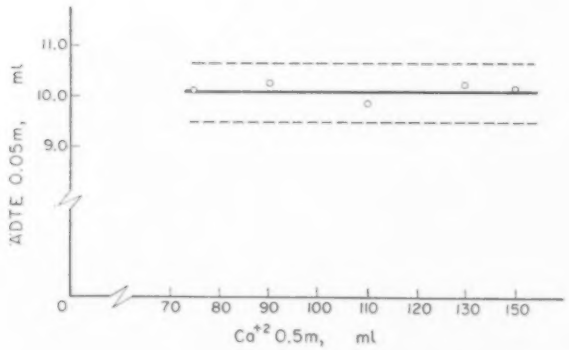

Abb. 2

Um zu überprüfen, ob die Gegenwart des gefallten Bariumsulfates die Magnesiumbestimmung mit ÄDTE merklich beeinflusst, haben wir einige Magnesiumbestimmungen im Filtrat der Bariumsulfat-Trennung durchgeführt. Die Ergebnisse sind aus Tabelle 3 ersichtlich.

Die Werte der Bestimmungen 1 bis 3 sind die Mittel von 5 Bestimmungen, die von 4 bis 7 von 3 Bestimmungen.

TABELLE III. BESTIMMUNG VON 12,16 mg MAGNESIUM IN GEGENWART WECHSELNDER CALCIUMMENGEN NACH VORHERGEHENDER FILTRATION VON $BaSO_4$

Ca^{+2} zugefuegt, *g*	Verhältnis Mg:Ca	0,05 m ÄDTE verbraucht, *ml*	Mg^{+2} gefunden, *mg*	Unterschied, *mg*
0,008	1:0,4	9,93	12,073	−0,087
0,040	1:2	10,02	12,182	+0,022
0,056	1:2,8	10,01	12,172	+0,012
0,150	1:7,5	9,98	12,141	− 0,021
0,200	1:10	10,04	12,203	+0,043
0,501	1:25	10,07	12,242	+0,082
1,002	1:50	10,12	12,301	+0,141

DISKUSSION

Aus der statistischen Berechnung der Ergebnisse jeder der beiden Reihen (Tab. 4 u. 5) kann man folgern, dass die Gegenwart von Ca im untersuchten Intervall keinen bestimmenden Einfluss auf die Ergebnisse der Magnesium-Titration mit ÄDTE hat,

TABELLE IV. ANALYSE DER VARIANZ FÜR DIE WERTE DER TAB. I UND ABB. 1

	Summe der Quadrate	Freiheitsgrade	Mittelwert der Quadrate	Berechnete Faktoren	Tabellisiert Faktor	Bedeutung
Wiederholungen	1,2281	4	0,3070	2,698	3,83	1%*
Behandlungen	0,8685	11	0,0789	0,693	2,70	1%†
Fehler	5,0055	44	0,1138			
Total	7,1021	59				

TABELLE V. ANALYSE DER VARIANZ FÜR DIE WERTE DER TAB. II UND ABB. 2

	Summe der Quadrate	Freiheitsgrade	Mittelwert der Quadrate	Berechnete Faktor	Tabellisiert Faktor	Bedeutung
Wiederholungen	0,5224	4	0,1306	0,360	4,77	1%‡
Behandlungen	0,5837	4	0,1459	0,402	4,77	1%‡
Fehler	5,8042	16	0,3624			
Total	6,9103	24				

* Zwischen 4 und 40
† Zwischen 10 und 50.
‡ Zwischen 4 und 16.

und man erhält als Ergebnis einen sicheren Grenzwert 0,167 der einen und 0,157 der anderen Versuchsreihe.

Wie sich aus den Ergebnissen der Tab. 1 und 2 ergibt, ist das Verfahren auf die Bestimmung von Magnesium in Gegenwart 150 mal grösserer Calciummengen anwendbar. Das bedeutet einen wichtigen Vorteil gegenüber den Verfahren, bei denen

man das Magnesium aus der Differenz erhält, denn wenn die Menge des vorhandenen Magnesium viel kleiner als die des Calcium ist, häufen sich in den Magnesium-Werten die Fehler von zwei Bestimmungen an, womit das Ergebnis wenig sicher wird und in gewissen Fällen, wie z.B. um ungenügende Mengen in Pflanzen festzustellen, ist der Magnesium-Wert viel wichtiger als der Calcium-Wert.

Anderseits hängt bei den Verfahren, in welchen das Calcium durch Fällung ausgeschieden wird, die Magnesiumbestimmung von einer vorhergehenden quantitativen Calcium-Trennung ab. Diese wird schwierig, wenn in der Lösung auch andere Jonen vorhanden sind, die bei dieser Trennung stören können. Man hat die Calcium-Trennung durch Fällung mit Oxalat, Molybdat oder Wolframat vorgeschlagen, doch ist bei all diesen Verfahren eine vorherige Entfernung des ausgefällten unlöslichen Calciumsalzes und ein gründliches Auswaschen der Niederschlages nötig um alles mitgerissene Magnesium zu entfernen.

Im vorgeschlagenen Verfahren wird eine Einwirkung des Calcium durch seine Maskierung in einem löslichen Komplex ausgeschaltet. So-mit wird die Bestimmung von Magnesium in Gegenwart von Calcium auf die Bestimmung von Magnesium in reiner Lösung zuruckgeführt.

Die Verfasser danken der Direktor von "Centro de Edafologia y Fisiologia Vegetal" (Santiago de Compostela) Herrn Prof. Dr. M Muñoz für die gegebene Hilfe und der Firma Geigy A.G. (Basel) für die überlassenen Muster von Chel De, die uns die Arbeit erleichtert hatten.

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Summary—The differences in the stability constants of the calcium, magnesium and barium complexes of EDTA and EGTA are used to develop a new volumetric determination of magnesium in the presence of up to a 150 fold excess of calcium.

$$Mg^{+2} + Ca^{+2} + Ba - EGTA \rightarrow Ca - EGTA + BaSO_4 + Mg^{+2}$$

The results of the titration are not significantly influenced by the presence of the barium sulphate precipitate.

Résumé—Les auteurs utilisent les différences des constantes de stabilité des complexes du calcium, du magnésium et du baryum avec l'EDTA et l'EGTA pour mettre au point un nouveau dosage volumétrique du magnésium en présence d'un excès de calcium plus de 150 fois plus important.

La présence de précipité de sulfate de baryum n'a pas d'influence signaficative sur les résultats du titrage.

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QUANTITATIVE PAPER RADIOCHROMATOGRAPHY USING TOLLENS REAGENT—I

THE APPLICATION OF ^{131}I TO RADIOMETRIC ESTIMATION OF MONOSACCHARIDES AND POLYOLS

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Summary—For the estimation of saccharides, a radiochromatographic quantitative method, based on the reaction with ammoniacal silver nitrate, has been developed. Conditions for the quantitative deposition of silver on the filter paper have been established. The silver deposit formed was transformed into $Ag^{131}I$. The radioactivity of ^{131}I located in the spots is related to the amount of the substance determined. The method has been checked using six substances, representing aldoses, ketoses, hexitols and cyclitols. The relationships between integrated spot activity, maximal spot activity and radiometrically estimated spot length, and the amount of substance have been studied.

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LABELLING directly on paper of chromatographically separated substances represents one of the recently developed techniques of quantitative microanalysis. Kaufmann and Budwig,[9] Winteringham *et al.*[17] and others have described some reactions of this kind carried out with simple radioactive reagents. Jaarma[8] suggested the possibility of using ^{110}Ag for the determination of aldoses and ketoses. Budzyński, Zubrzycki and Campbell in this laboratory have developed a method for the radiochromatographic determination of unsaturated fatty acids. This method is based on an addition of ^{131}I to double bonds.[3,4] The same authors have put forward a more complicated technique called by them "double decomposition radiochromatography". In this procedure, the labelling of chromatograms is carried out in two steps. The first one is a reaction of the substance being determined with a non-radioactive ion; the latter, in the second step, combines with the radioactive tracer.[4,18]

In the present paper a new series of transformations which allow the radiometric determination of chromatographically separated substances will be described.

In a search for systems suitable for the determination of various reducing compounds, attention was drawn to ammoniacal silver nitrate, the so-called Tollens reagent. This reagent, commonly used in qualitative chromatography, is characterised by a high sensitivity, and the ability to react with a wide variety of compounds. As the result of such reactions elementary silver is deposited on the paper. The use of silver, because of its physical and chemical properties, and also because of its ability to form numerous sparingly soluble compounds, proved to be especially advantageous. The chemical affinity of elementary silver for iodine is marked, and the rate of the reaction between the two elements depends mainly on the state of dispersion of the reactants.[1,12,15] Examination of this reaction, using an aqueous solution of ^{131}I, resulted in the working out of the conditions necessary for the quantitative formation of $Ag^{131}I$ from a silver deposit on the paper.

The application of these transformations to the quantitative radiochromatography of monosaccharides and polyhydric alcohols is described below.

EXPERIMENTAL

Reagents

Monosaccharides and polyhydric alcohols: Glucose, xylose, rhamnose, fructose, mannitol and inositol; commercial preparations, analytical grade were used in all experiments.

Ammoniacal silver nitrate: Solutions used in paper chromatography usually contain from 1·7% to 5% of $AgNO_3$.[2,6,7,10,13,16] It was found that this range of concentrations is insufficient for the quantitative oxidation of more stable substances. Therefore solutions containing 9–17% of silver nitrate in concentrated ammonia were used in these experiments. Sodium hydroxide, which accelerates the reaction was found to be an indispensable component of these solutions. Several reagents of different composition were tested. Two of them which ensure the quantitative course of the reaction and give comparatively low background have been chosen. The composition of these solutions is given in Table I.

TABLE I. AMMONIACAL SILVER NITRATE SOLUTIONS. COMPOSITION AND REACTION TIME FOR SILVER DEPOSITION

Silver nitrate, g	8·5	15·0
Sodium hydroxide, g	0·3	0·1
Ammonia 25%	up to 100 ml	
Heating time for chromatograms at 105°, min	25	15

Chromatography

Whatman No. 1 paper strip chromatograms, 350 mm long and 15 mm wide, were prepared. The substances to be tested, in amounts of $1{\cdot}5 \times 10^{-2} - 60 \times 10^{-2}$ μM, were put on the starting point located 60 mm from the lower end of the strip. The chromatograms were developed by the ascending technique for 18 hr at room temperature, using the system n-butanol:acetic acid:water = 6:1:2.[11] Before further operations the chromatograms were air-dried for 24 hr.

Deposition of elementary silver on paper

Chromatograms were placed horizontally on specially designed racks and sprayed. Fifteen mg of the solution applied to 1 cm² of the paper was found to be a sufficient excess for the quantitative course of the reaction. Full details of the spraying technique will be published elsewhere.

Wet chromatograms were transferred on racks to the oven and heated at 105°. The optimal heating time is given in Table I. These reaction conditions cause the formation of dark-brown or black spots on a dark-yellow background. It is recommended that the conditions should not be changed so as to obtain a less intense background since this prevents the quantitative deposition of the silver.

Immediately after deposition of silver, excess of Tollens reagent was removed using 0·02% aqueous ammonia. The strips were washed with this solution for 2 min, then with water three times for 5 min, and finally air-dried.

Transformation of elementary silver into $Ag^{131}I$

One hundred ml of a solution containing 0·4 g of potassium iodide and 0·02 g of potassium iodate were added to 300 μC of carrier-free $K^{131}I$. Free iodine was liberated from this solution by 0·4 ml of 10% sulphuric acid just before use. Ten ml of this reagent can transform on paper into iodide an amount of silver equivalent to 50 μg of glucose in 20 min.

The reaction was carried out in vertical paraffin vessels of slit-like cross-section,[4] 4 mm × 16 mm for 60 min. The iodinated strips were washed with water three times for 5 min.

Estimation of activity on strips

The distribution of activity on air-dried radiochromatograms was estimated using an end-window counter, with a mica-window 4 mg/cm². The chromatograms were placed under the 4-mm thick Perspex screen. A 2-mm slit cut in the screen allowed counting of β-particles from a defined area of the chromatogram.

RESULTS

The technique described was applied to the radiochromatographic determination of the following typical representatives of different classes of monosaccharides and polyols: glucose, xylose, rhamnose, fructose, mannitol and inositol.

Typical results for the activity estimation of a radiochromatogram prepared in such a way are presented graphically in Fig. 1.

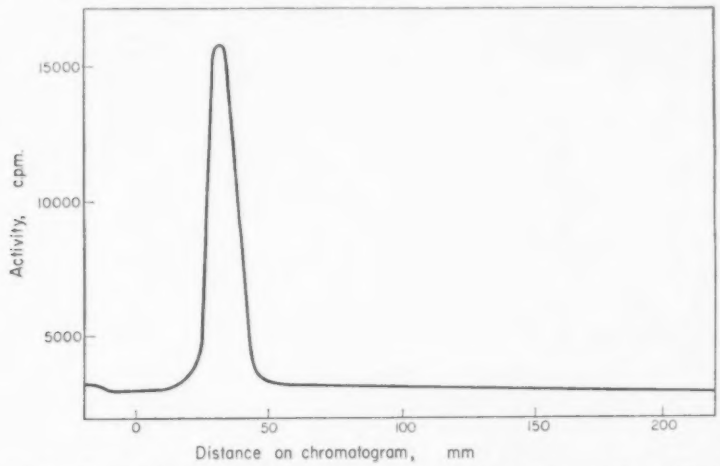

FIG. 1.—Distribution of activity on chromatogram of 100 μg of glucose after $Ag^{131}I$ formation in place of sugar.

The integrated spot activity, *i.e.*, the sum of activities estimated from individual 2-mm sectors of the strip, minus background activity, was calculated as the main parameter. The linear relationship between this parameter and the amount of chromatographed substances is presented in Figs. 2 and 3. The ranges for which this regularity was proved and the average errors of determinations are listed in Table II. Although in every case it was possible to determine as little as $1{\cdot}5 \times 10^{-2}$ μM, it was found that these determinations were accompanied by considerable errors ranging from $\pm 8\%$ to $\pm 23\%$. The average error for amounts larger than 10×10^{-2} μM was $\pm 3{\cdot}5\%$ to $\pm 7{\cdot}6\%$.

TABLE II. REGION OF PROPORTIONALITY BETWEEN INTEGRATED SPOT ACTIVITY AND AMOUNT OF SUBSTANCE, AND AVERAGE ERRORS OF THE METHOD FOR AMOUNTS HIGHER THAN 10×10^{-2} μM

Substance	Region of proportionality, $\mu M \times 10^{-2}$		Average error for amounts higher than 10×10^{-2} μM
	from	to	
Glucose	1·5	60	±6·7
Xylose		45	±7·6
Rhamnose		60	±5·5
Fructose		30	±3·5
Mannitol		30	±5·7
Inositol		23	±4·3

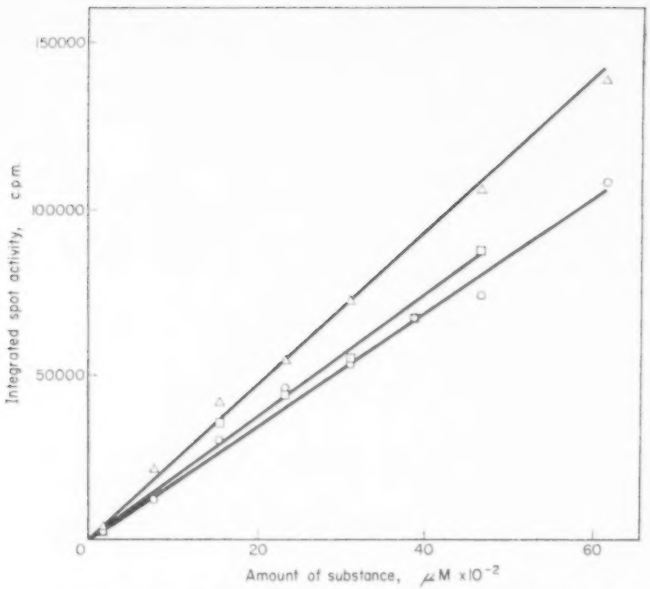

FIG. 2.—Relationship between integrated spot activity and amount of substance: ○ — glucose, □ — xylose, △ — rhamnose.

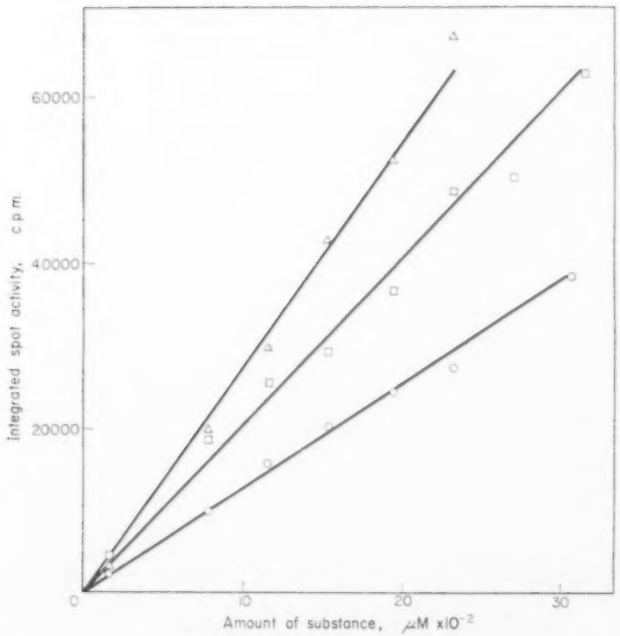

FIG. 3.—Relationship between integrated spot activity and amount of substance: ○ — fructose, □ — mannitol, △ — inositol.

It is necessary, in order to analyse chromatographically separated mixtures, to set up calibration curves based on simultaneously performed determinations of known amounts of the corresponding standard substances. Because of the character of the relationships presented, it is sufficient to estimate only one point on the curve.

For the quantitative determinations of saccharides, other parameters that characterise the spots can be also used. The linear relationship between maximal spot activity and the logarithm of spot content has previously been observed in the case of radiochromatographic determinations of saturated and unsaturated fatty acids and inorganic phosphates.[4,18] This relationship was tested for all the sugars and alcohols examined. Fig. 4 shows the relationship between maximal spot activity (*i.e.*, maximal activity determined on the 2-mm segment of the strip) and the logarithm of spot content.

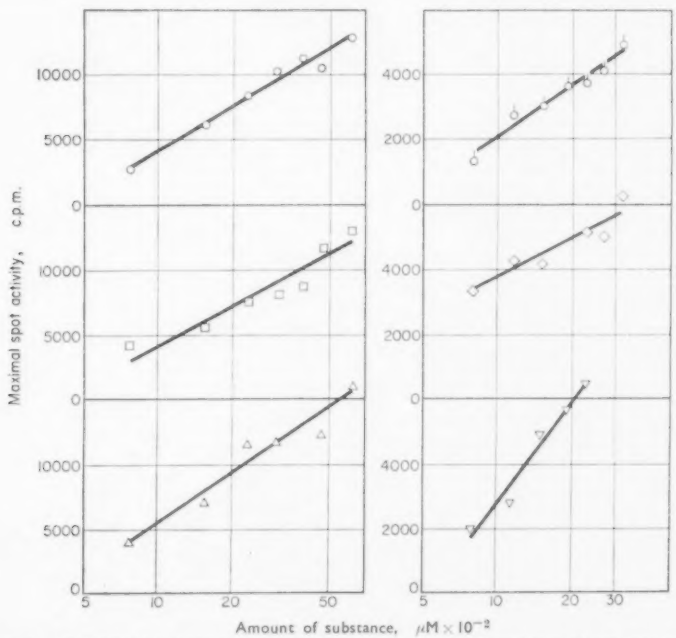

FIG. 4.—Relationship between maximal spot activity and logarithm of amount of substance: ○ — glucose, □ — xylose, △ — rhamnose, ⬡ — fructose, ◇ — mannitol, ▽ —inositol.

The distribution of activity on a labelled chromatogram can serve as a basis for the determination of spot length.[4,18] The parameter calculated in such a way is directly proportional to the quantity of the chromatographed substance. Fig. 5 shows the relationship between the radiometrically determined spot length and the amounts of sugars and alcohols examined.

Maximal spot activity, as well as spot length, can be used as a basis for rapid determinations which do not require activity measurements along the whole spot length. The minimal amount of substance that gave the linear relationships mentioned was $7{\cdot}5 \times 10^{-2}\ \mu M$. The average error of determinations based on maximal spot activity measurement usually ranged from $\pm 8\%$ to $\pm 13\%$, and of those based on spot length from $\pm 8\%$ to $\pm 15\%$. Maximal spot activity measurement seems to be particularly useful for the determination of substances overlapping on chromatograms.

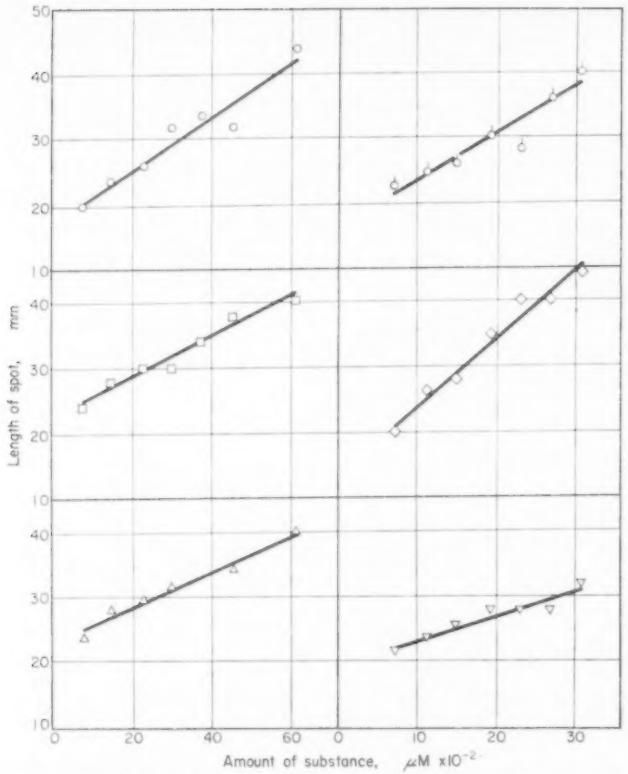

FIG. 5.—Relationship between radiometrically estimated spot length and amount of substance: ○ — glucose, □ — xylose, △ — rhamnose, ⌀ — fructose, ◇ — mannitol, ▽ — inositol.

DISCUSSION

The results described above prove that transformations with simple radioactive reagents, carried out on paper, can be applied to the quantitative chromatography of saccharides and related compounds. The chemical properties of the substances used in these experiments permit one to make the assumption that the technique, if properly elaborated, could have a general application to all monosaccharides, aldoses as well as ketoses, and to all chain and cyclic polyols. Other compounds related to sugars, *e.g.*, uronic acids, amino-sugars, alkylated sugars, lactones, esters, amides and glucosides also give a positive Tollens reaction.[7] The results obtained with compounds which react slowly with ammoniacal silver nitrate, such as mannitol and inositol, indicate that this technique can be applied here also.

Most of the known methods for the determination of sugars and related compounds permit the analysis only of compounds which belong to definite chemical groups. It is well-known that the determination of more stable, so called non-reducing compounds presents one of the more difficult analytical problems. Therefore it would be very convenient to possess a method which would allow the determination of a wider variety of compounds, separated on a single chromatogram. Such a method could be used for estimation of the sugar components of glucosides, glucoproteins, *etc.*, as well

as for examination of polysaccharides. No existing methods allow such complex analyses to be performed directly on paper chromatograms.

The estimation of the silver deposited on paper can be also performed by optical methods. McFarren *et al.*[10] and Wallenfels *et al.*[16] elaborated methods for the determination of aldoses on the basis of such measurements. The determination of more stable compounds, however, encounters serious difficulties connected with more drastic reaction conditions required, which lead to the oxidation of paper cellulose. The dark background that is formed under such conditions prevents densitometric evaluation of the chromatograms. In the application of radiometric techniques, side reactions which take place along the whole chromatogram do not interfere basically. The use of β-emitters whose energy is sufficiently high eliminates the difficulties connected with variations in the thickness of the filter paper, which are the main source of errors in photometry.

The deposition of elementary silver on paper, and its transformation into $Ag^{131}I$, might also be applied to the determination of other groups of chemical compounds. In addition to various kinds of saccharides, the following substances react with Tollens reagent: aldehydes, polyhydroxyphenols, aminophenols, hydroxycarboxylic acids, α-diketones, primary ketols, sulphinic acids, certain aromatic amines, hydrazo compounds, hydrazines, hydroxylamines, *etc.*[5] The technique described may find an application in the radiochromatography of these compounds, provided that the conditions for quantitative deposition of silver are established.

Acknowledgements—The author is greatly indebted to Professor Irena Chmielewska and Professor Edward Kowalski for their helpful discussion.

The technical aid of Mr. Wladyslaw Telakowski is gratefully acknowledged.

Zusammenfassung—Eine quantitative radiochromatographische Methode zur Bestimmung von Monosacchariden und Polydroxyalkoholen wurde entwickelt. Sie beruht auf der Reaktion von ammoniakalischer Silbernitrat lösung mit den zu bestimmenden Substanzen. Die Bedingungen für quantitative Präzipitation des Silbers wurden bestimmt. Der so erhaltene Niederschalg wurde in $Ag^{131}J$ umgewandelt. Es wurde nachgewiesen daß die Radioaktivität des ^{131}J als Maß des Gehaltes der zu bestimmenden Substanzen dienen kann. Die Methode wurde nachgeprüft für sechs verschiedene Substanzen, die Aldosen, Ketosen, Hexite und Cyclite repräsentieren. Es wurden die Beziehungen zwischen der Menge der Substanz und der Gesammtaktivität der Flecken, ihre maximale Aktivität und die radiometrisch bestimmte Länge des Fleckes untersucht.

Résumé—On a élaboré une méthode de la radiochromatographie quantitative pour la détérmination des glucides. Cette méthode est basée sur la réaction du nitrate d'argent ammoniacal donnant le précipité d'argent élémentaire. On a établi les conditions de la déposition quantitative d'argent sur le papier. Le précipité ainsi obtenu a été transformé en $Ag^{131}J$. On a démontré, que la radioactivité de ^{131}J deposée sur les radiochromatogrammes peut servir pour détérminer des quantités des substances dosées. La méthode décrite a été verifiée sur des exemplaires des six substances représentatives pour les aldoses, cétoses, hexitols et cyclitols. On a étudié les rélations entre la quantité de la substance dosée, et l'activité totale de la tâche, la maximum d'activité de la tâche, et la longueur de la tâche, determinée radiométriquamment.

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A UNIVERSAL AUTOMATIC RECORDING TITRATOR*

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Summary—A universal automatic macro-micro recording titration unit is described which has the capabilities of a multitude of commercial single-purpose titration instruments without the attendant duplication of hardware. It is based on a modified Precision Dow Recording Titrator and offers the operator a choice of liquid or coulometrically generated titrants and potentiometric, amperometric, thermometric, photometric, or conductometric end-point detection systems.

The potentiometric system gives straightforward curve-presentation; the photometric mode employs a monochromator for maximum sensitivity and is equally adaptable to colorimetric, turbidometric, and chemiluminescent titrimetry; the conductometric mode employs a novel electrolytic conductivity transducer which produces a d.c. signal proportional to the 60-cycle a.c. current between the electrodes. All components are easily constructed or are commercially available.

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INTRODUCTION

IN recent times, the discovery of new and useful techniques of analytical chemistry has been followed, not long after, by the availability of commercial instrumentation designed to utilise the technique and impart to it such well-recognised advantages of instrumentation as improved accuracy, sensitivity, specificity, operating economy, *etc.* For the small analytical control or research laboratory, the availability of such instrumentation is a mixed blessing; while its use enables the laboratory to operate more efficiently and to cope with a broader range of analytical problems, the acquisition of much of this instrumentation results in an astonishing duplication of instrument components with attendant expense and storage problems.

Since automatic titrating instruments form the bulk of available laboratory instrumentation, and since the analytical chemist is becoming increasingly dependent upon end-point phenomena which are detectable only by instrumental means, it seemed probable that considerable progress in the versatilisation of existing commercial laboratory instruments could be made in this area. The authors have, therefore, assembled an automatic macro-micro recording titration unit which has the capabilities of a multitude of commercial single-purpose titration instruments without the attendent duplication of hardware. A Precision Dow Recording Titrator provides titrant delivery, end-point anticipation, and curve recording functions and is utilised, unmodified, for potentiometric end-point detection. Commercially available or easily constructed add-on components are used for coulometric generation of titrant and for detection of conductometric, photometric, amperometric, and thermometric end-points. Fig. 1 shows a titrator equipped for all but photometric end-point detection; the photometric titrator is pictured in Reference 5. Fig. 2 shows the block diagram of all components in relation to the Precision Dow Titrator.

Conductometric titration capability is unique to this titrator and permits the

* This paper was presented at *The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy*, February, 1961.

chemist to utilise the well-known advantages of conductometric titrimetry over potentiometric titrimetry, while retaining automatic operation. Recently, a single purpose automatic conductometric titrator was described by Colvin and Propst,[1] but the conductance bridge described in the present paper can be adapted for use with any automatic potentiometric recording titrator. Photometric titration capability is broader than that found in most available instruments and includes provisions for

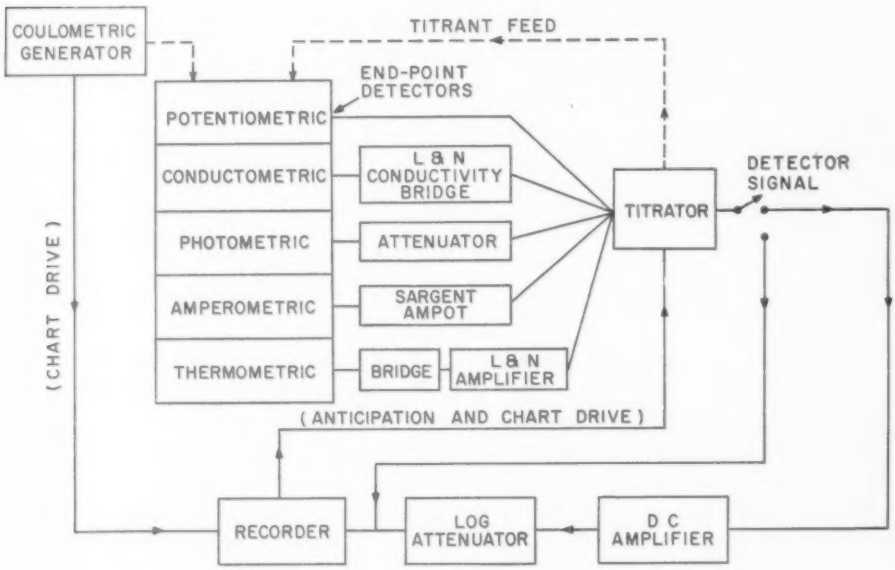

FIG. 2.—Block diagram for universal automatic recording titrator.

end-point detection using visual, near ultraviolet and fluorescent indicator systems; a monochromator is utilised, making the unit particularly adaptable to sensitive and precise mixed indicator end-points.

Dead-stop methods of titration terminations are not used; rather the complete titration curve is drawn leaving the analyst free to inspect the titration system for unexpected behaviour, locate end-points on asymetrical curves, *etc.* Although dead-stop methods could be employed, the full-curve technique has proved its value repeatedly in non-control analytical work.

EXPERIMENTAL

Potentiometric end-point titrator

The Precision Dow Recording Titrator, a commercial version of the instrument described by Robinson,[5] is designed for use only with potentiometric titrations. The unit essentially consists of the titrant-delivery system, recorder and potentiometric indicating system.

The delivery system normally comprises two separate 1-, 5-, or 50-ml precision-bore glass feed pumps, glass titrant delivery lines with burette tips, three-way stopcocks and syphon tubes. The selection of either the right or left feed system is accomplished by manually shifting the selector knob on the control panel.

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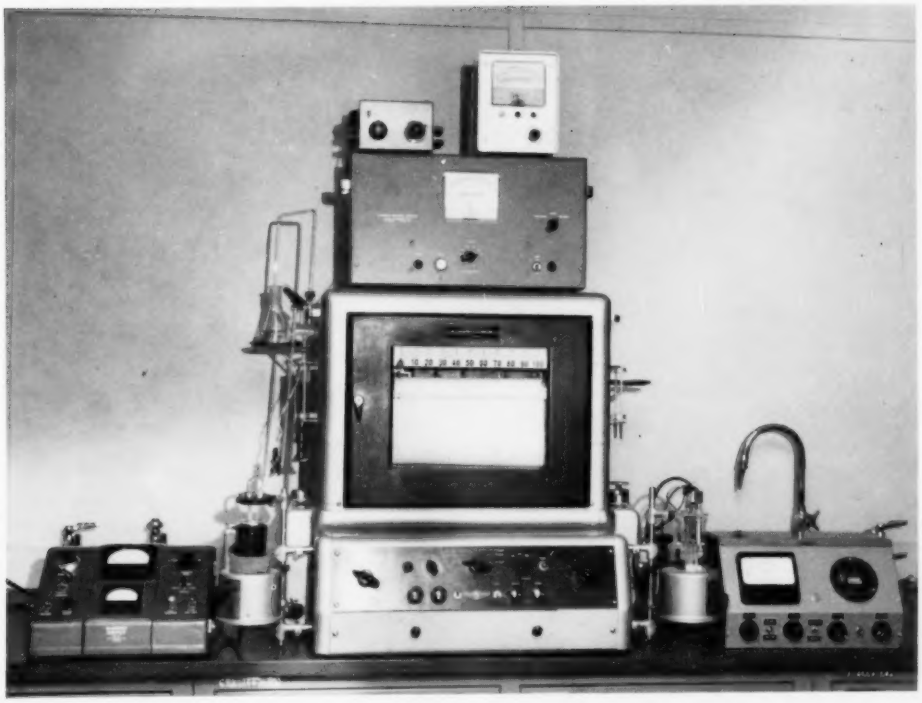

FIG. 1.—Universal automatic recording titrator

Centre: Precision Dow Automatic Recording Titrator;
Right: Coulometric generator;
Left: Sargent Ampot;
Top centre: Leeds and Northrup Microvolt Amplifier;
Top left: bridge circuit for thermometric titrations;
Top right: Leeds and Northrup Conductivity Bridge.
The thermometric titration cell is shown on the left and the coulometric titration cell shown on the right of the Precision Dow Titrator.

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The plunger of the feed pump is automatically driven by a relay-operated motor with the feed rate being adjustable to a maximum of 3 ml per min. The upper limit of plunger travel is controlled by a limit switch which protects the feed pump and other glassware from damage. If titrant should run low during a titration, the feed pump may be refilled and the titration resumed without the loss of the sample.

Because the titrant feed and chart advancing systems are mechanically linked, the chart reflects the actual amount of titrant added. One major chart division (approximately 23 mm) equals 1, 0·2, or 0·05 ml of titrant, depending on which feed pump is used.

The 22-sec 1 mV Brown Electronik Potentiometer furnished with the Precision-Dow instrument is an especially modified, 6-range, unit. A balanced-tube vacuum tube voltmeter links the titrator circuit to the potentiometer and allows only equilibrium values of e.m.f. to be plotted. When an e.m.f. change of as little as 5 mV occurs in the input to the titrator, the potentiometer is instantaneously unbalanced, and a feed control relay cuts off the feed motor and the chart drive until both the input e.m.f. and the potentiometer are again in balance. In this manner, fairly constant titrant addition is maintained during the early stages of a titration, when buffer action is strong, while additions become more widely spaced as buffer action is reduced.

The motor driving the feed system is equipped with a friction brake which allows close control of the incremental reagent additions.

Conductance end-point titrator

Automatic recorded conductance titrations can be performed by using a modified Leeds and Northrup Model 4958 conductivity bridge in conjunction with the Precision-Dow Titrator. The conductivity bridge is a small, portable instrument, which provides manual and/or automatic temperature compensation and produces a d.c. signal proportional to the conductivity of the solution in which the electrodes are immersed. A stabilised a.c. voltage of known value (obtained from a constant voltage transformer) is applied to the electrodes, resulting in a current flow that is directly proportional to the conductivity of the solution. The magnitude of the resultant current is measured by connecting a resistance circuit of relatively low impedance in series with the cell to obtain an a.c. signal proportional to the current. The a.c. signal is then coupled to a transistorised demodulator by a coupling and isolating transformer. The rectified output of the demodulator is measured by a d.c. microammeter. A 0–10 mV d.c. signal for operating a recording instrument is obtained from a precision

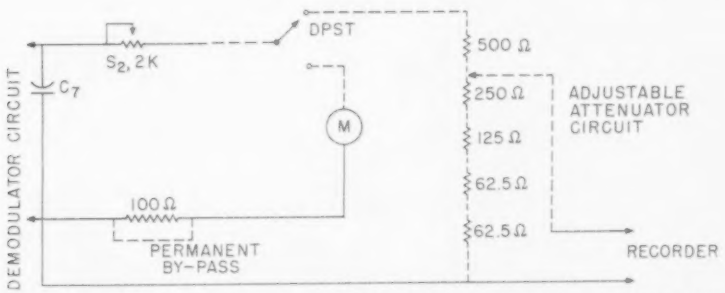

FIG. 3.—Modifications to the Leeds and Northrup Conductivity Monitor, Model 4958.

Modifications shown as broken lines
Other components shown:

S_2: 2K-potentiometer
C_7: 50 μF(Std. 2645–53)023213 capacitor
M: 0–100 microammeter

resistor connected in series with the d.c. microammeter. However, the Brown recorder in the Precision-Dow has a range of 0–50 mV so that the nominal full-scale signal from the bridge would be only 1/5 the full-scale range of the recorder. Therefore, it was necessary to modify the bridge to accommodate the recorder in the Precision-Dow Titrator. This modification is given in Fig. 3. The 0–100 microammeter employed in the conductivity monitor has a 1000 Ω internal resistance, and with the 100-Ω precision resistor connected with it in series, gives a full scale d.c. signal of 0–10 mV. In

the modification, the 100-Ω precision resistor was by-passed, and a double pole single throw (DPST) switch was incorporated to permit operation of the recorder through an attenuator circuit containing resistance totalling 1000 Ω. The recorder leads are tapped across 500 Ω, giving a signal range of 0–50 mV to accommodate the recorder. By switching to the proper additional attenuator resistor, one can effectively change the recorder full scale from 50 to 400 mV without further adjustment. This is an important feature, since many conductance titrations have varied initial conductance readings. For relatively high conductance, one is forced to work in a region of higher voltage output from the monitor, thereby requiring an adjustment in the total resistance to get the signal on the recorder scale.

A second modification was needed to introduce the bridge output directly to the recorder in the titrator. This was accomplished by mounting a double pole double throw (DPDT) switch on the terminal board inside the recorder housing. With the switch in one position, the bridge is wired directly into the recorder input, while the switch in the opposite direction allows for normal operation of the Precision-Dow Titrator. When using the recorder as part of the conductance titrator, the anticipation circuit of the titrator is still available, since the recorder amplifier, and not the titrator detector circuit itself, is the sensitive element in the anticipation circuit.

Prior to operation, the potentiometric indicating electrodes on the Precision-Dow are replaced by a conventional conductivity electrode. The electrode leads are connected to binding posts located in the back of the Leeds and Northrup bridge, and the monitor is connected to the recorder through the DPDT switch previously described. A solution containing the sample and a "Teflon"*-covered magnetic stirring bar is positioned on the magnetic stirrer and the electrodes immersed so that the burette tip and the electrodes are below the surface of the liquid. Stirring should be adequate but not sufficiently vigorous to allow an air cavity to form in the vicinity of the electrodes. The recorder, which is set at the ±1-V range with the position selector knob at zero, is turned on and the pen brought on scale by using the attenuator control mounted in the back of the monitor. This instrument has a linear range up to 800 μmhos. The dilution effect common to conductometric titrations can be minimised by using a micro-titration pump. Temperature control has not been found necessary.

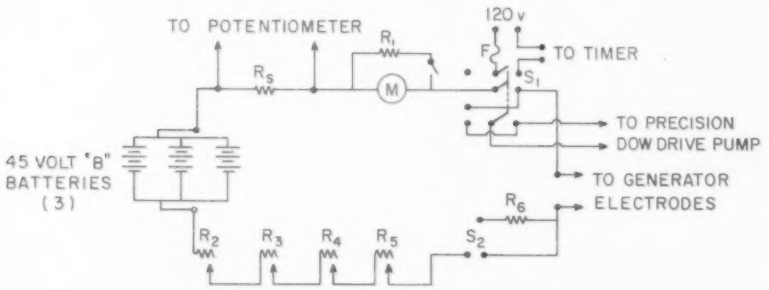

FIG. 4.—Electrical circuit for coulometric analyser

M: milliammeter 0–10 0–100 mA, calibrated
R_1: resistor 0·63 Ω
R_2: 10-Ω 4-W wire wound variable resistor
R_3: 100-Ω 25-W wire wound variable resistor
R_4: 1000-Ω 50-W wire wound round variable resistor
R_5: 5000-Ω 25-W wire wound variable resistor
R_6: 5000-Ω 25-W wire wound fixed resistor
R_s: resistor of a measured value (standard), in this circuit, the resistor measures 9·716 Ω
F: fuse, 2 A 250 V
S_1: TPDT centre off switch
S_2: SPDT switch

Photometric end-point titrator

Titrations requiring photometric end-point detection can be performed by using a Precision-Dow Titrator modified in a manner recently described by the authors.[4] Briefly, the modification comprises a Beckman Model B spectrophotometer with a specially designed compartment for the titration cell and a logarithmic attenuator, which seems to produce a signal from the spectrophotometer which is

* Trademark for du Pont's tetrafluoroethylene resin.

proportional to the solution absorbance. The normal titrant delivery tube and burette tip supplied with the titrator is replaced by one which leads directly from the feed pump to the modified cell compartment of the spectrophotometer. The titrator is suitable for colorimetric, nephelometric, and fluorescent indicator titrimetry. The modified cell compartment is provided with a hydrogen lamp as an ultraviolet source for fluorescent indicator titrimetry.

Coulometric titrator

The Precision-Dow Titrator can be modified to perform coulometric titrations by the addition of a relatively inexpensive battery operated constant current source. The circuitry (Fig. 4) for the constant current source is a modification of the one given by Cooke and Furman.[2] Three 45-V "B" batteries are used as the source of current, and an electric timer is included in the circuit in such a way that when the current is turned on, the timer and the recorder, or the recorder alone, in the titrator is turned on simultaneously. The calibrated milliammeter M can be made to read 10 or 100 mA at full scale by closing or opening the shunt resistor R_1 to the generating current. The generating current is adjusted by simple manipulation of the variable resistors in the circuit. These resistors are of the high wattage type so that they operate with relatively little temperature rise. A calibrated resistor, Rs, is included in the circuit for the purpose of checking out the circuit with a potentiometer. It was found that if three 45-V "B" batteries are connected in parallel, the current decreases less than 0·2% for a 10-min operating period at 10 mA. The chart is actuated when the current is turned on by making a jumper connection to the titrant pump motor relay from the constant generator as illustrated in Fig. 4. In this application, the titrant delivery glassware and the pump on one side of the titrator are completely removed, and a suitable holder containing the indicating and generating electrodes necessary for a particular run are mounted in the normal position over the magnetic stirrer as illustrated in Fig. 1. For example, in titrating acids, the hydroxyl ion was generated from a platinum cathode with the platinum anode isolated in a glass tube containing 10% sodium sulphate in agar gell and sealed at the end exposed to the solution with a sintered glass disc. The supporting electrolyte was 5% sodium sulphate in water and the titration was followed with glass-calomel electrodes. By disengaging the jaw which connects the titrant pump and the pump motor, the feed control can still be used and the forward movement of the chart controlled. The chart is calibrated in mequiv. per chart division by allowing the chart and timer to run simultaneously at a specified current and a fixed chart speed setting. Once the calibration has been made, a titration can be conducted without using the timer.

Amperometric end-point titrator

Coulometric titrations usually employ the dead-stop or amperometric end-point detecting system. The Precision-Dow Titrator can be modified to automatically record amperometric end-points by simply running a jumper connection from the binding posts of the microammeter in a Sargent

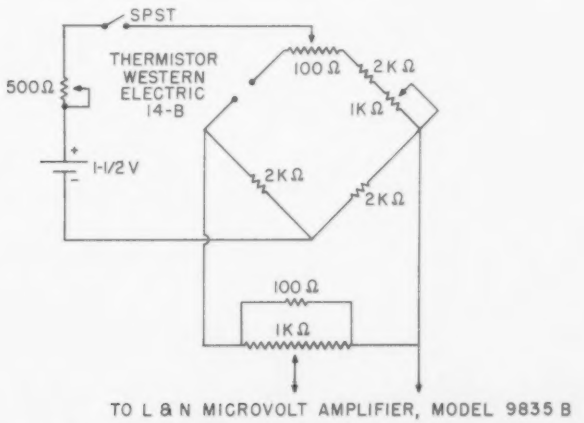

FIG. 5.—Bridge circuit for automatic recording thermometric titrator.

"Ampot" directly into the titrator recorder. This setup can be successfully used, for example, to standardise a solution of sodium thiosulphate by coulometrically generating iodine from potassium iodide. Two micro platinum electrodes can be used to detect the end of the titration.

Thermometric end-point titrator

Thermometric end-points have been achieved with this titrator using a technique similar to that described by Linde, Rogers and Hume.[3] A Western Electric 14B glass enclosed thermistor is ganged into a Wheatstone bridge powered by a 1·5-V battery (Fig. 5). Two variable resistors constituting the coarse and fine zero adjustments are included in the bridge circuit. The output from the bridge, which can be controlled by the variable span resistor, is fed into a Leeds and Northrup Model 9835B Microvolt Amplifier which has an imput range from 50 to 2000 mV and a 10 and 50 mV full-scale output for each input range. The output from the amplifier is fed directly to the input of the 50 mV Brown recorder in the Precision Dow Titrator. Gross changes in thermistor response caused by sudden changes in temperature will activate the attenuator circuit, stopping the flow of titrant until the system has equilibrated. Titrations were carried out in a small Dewar flask as shown to the left in Fig. 1.

DISCUSSION

Performance

The automatic recording coulometric titrator can be adapted for any type of titration that can be performed by constant current coulometric techniques provided the proper generating and indicating electrodes are used. Plot *A* in Fig. 6 illustrates the type of curve obtained when titrating 0·01 mequiv. of phosphoric acid with coulometrically generated hydroxyl ions. It was found that a precision of better than ±1 % was achieved when titrating 0·01 mequiv. of hydrochloric acid with coulometrically generated hydroxyl ion at a current density of 5 mA. Actually, titrations can

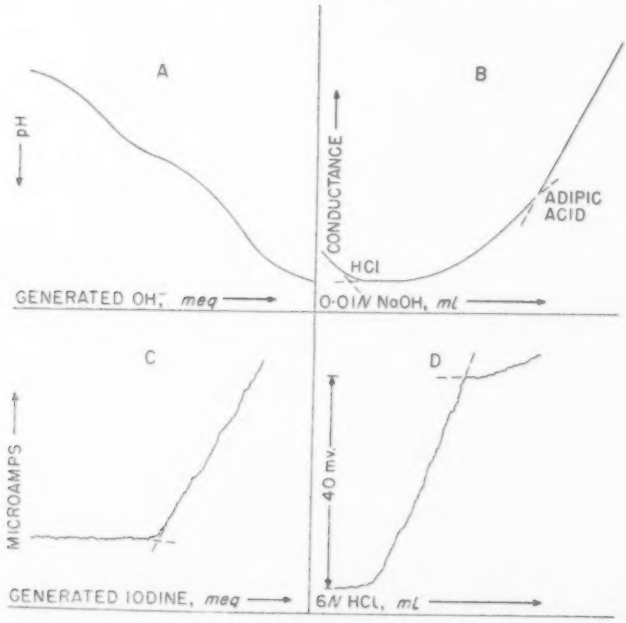

FIG. 6.—Typical titrations.
A: coulometric titration of phosphoric acid
B: conductometric titration of hydrochloric acid and adipic acid
C: coulometric titration of sodium thiosulphate illustrating amperometric end-point
D: thermometric titration of sodium hydroxide

be carried out at a current of 20 mA before noticeable interaction between generating and indicating electrodes are encountered. Plot *B* represents the automatic conductometric titration of 0·065 mequiv. of adipic acid in the presence of 0·015 mequiv. of hydrochloric acid. The estimated precision obtained in determining 0·065 mequiv. of adipic acid is about ±2·9%, compared to ±5% for the same concentration by manually plotting the data. Plot *C* represents the titration of 0·01 mequiv. of sodium thiosulphate with coulometrically generated iodine (from potassium iodide) to an amperometric end-point. Plot *D* illustrates the thermometric titration of 0·6 mequiv. of sodium hydroxide with 6·0*N* hydrochloric acid. The slight upward drift in the curve is caused by the stirring action and other background effects.

Acknowledgment—The aid given to this work by C. P. Krula, Central Research Department, who designed the electronic circuitry for the required modifications is gratefully acknowledged.

Zusammenfassung—Eine universelle Makro-Mikro-Titrationseinheit für automatische Titrationen wurde beschrieben. Das Gerät ist eine Modifikation des Dow-Präzisions-Titrationsschreibers und erlaubt Titrationen mit Masslösungen, culometrisch erzeugten Reagenzien und kann zur potentiometrischen, amperometrischen, thermometrischen photometrischen oder konduktometrischen Endpunktbestimmung herangezogen werden.

Die potentiometrische Titration kann sowohl wie üblich als aüch in zweiter Ableitung durchgeführt werden. Die photometrische Einheit enhält einen Monochromator zur Erhöhung der Empfindlichkeit und kann auch für nephelometrische, turbidimetrische und fluorometrische Titrationen eingesetzt werden. Der konduktometrische Teil enthält einen neuartigen elektrolytischen Leitfähigkeitstransducer, der ein Gleichstromsignal erzeugt, des deru Wechselstrom von einer Frequenz 60 zwischen den Elektroden proportional ist. Alle Teile sind leicht herzustellen oder käuflich erwerbbar.

Résumé—Les auteurs décrivent une unité de titrage universelle automatique pour les dosages, avec enregistrement. Cette unité offre les possibilités d'un grand nombre d'appareils de titrage commerciaux simples sans l'inconvénient d'en avoir plusieurs.

Elle est basée sur un titrimètre enregistreur modifié "Précision-Dow" et offre à l'opérateur un choix de liquides ou de réactifs titrants préparés par coulométrie, ainsi que différentes méthodes pour décaler le point équivalent: potentiométrie, ampérométrie, thermométrie, photométrie ou conductimétrie.

La méthode potentiométrique offre le choix pour présenter la courbe, soit directement, soit en passant par la dérivée seconde; la méthode photométrique emploie un monochromateur pour avoir une sensibilité maximale, celui-ci est également adaptable aux titrimètries colorimétrique, turbidimétrique, chimioluminescente; la méthode conductimétrique emploie un nouveau système qui produit un signal continu proportionnel au courant alternatif de 60 périodes entre les électrodes. Tous les constituants de l'appareil sont facilement construits ou sont disponibles.

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NEW REDOX SYSTEMS—IV*

OXIDATION OF COBALT^{III} WITH IRON^{II} CHLORIDE IN 2,2′-BIPYRIDYL

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Summary—The oxidation of cobalt^{II} with iron^{III} chloride in the presence of 2,2′-bipyridyl has been studied potentiometrically and colorimetrically. The course of this reaction corresponds to a previously studied redox reaction in which 1,10-phenanthroline was used as the complex forming reagent. The formal redox potentials of the studied reaction have been calculated and their dependence on the concentration of 2,2′-bipyridyl and pH values studied. The possibility of utilisation of this redox system for the determination of cobalt is discussed.

IN previous papers of this series[1,2] it was reported that cobalt^{II} can be oxidised with iron^{III} chloride in the presence of 1,10-phenanthroline. This reaction was subsequently used for the direct potentiometric determination of cobalt with iron^{III}.[3] The determination of the concentration of ferroïn, which is formed during this reaction, allows the indirect determination of cobalt. Large quantities of ferroïn (cobalt) can be determined cerimetrically,[4] very small quantities colorimetrically.[5] Recently, this reaction has been used for the amperometric determination of cobalt.[6] For the oxidation of cobalt^{II} with iron^{III} it is possible to replace 1,10-phenanthroline by 2,2′-bipyridyl and the course of the reaction is

$$(Co^{II})_{Bip} + (Fe^{III})_{Bip} \rightleftarrows (Co^{III})_{Bip} + (Fe^{II})_{Bip} \qquad (1)$$

As would be expected, the mechanism and the optimal conditions of this reaction are practically identical with the similar system involving 1,10-phenanthroline. From the potentiometric data the formal redox potentials of the participating redox systems were calculated and their dependence on the concentration of complex forming reagent and pH studied.

EXPERIMENTAL

Reagents

0·01 M cobalt^{II} nitrate and 0·01 M iron^{III} chloride solutions: Prepared from reagent grade chemicals. 0·001 *M* cobalt^{II} nitrate solution was prepared from the 0·01 *M* solution by suitable dilution. The titre of these solutions was controlled gravimetrically.

0·01 M 2,2′-bipyridyl solution: Prepared by dissolving 1·5618 g of analytically pure substance in 1 litre of water, weakly acidified with hydrochloric acid (resulting pH value 3).

Buffer solutions: Prepared by neutralisation of the calculated quantity of chloracetic acid or acetic acid with aqueous ammonia to the necessary pH, while a potentiometric control was maintained with a glass electrode. The resulting molarity of the solutions was 1.

Apparatus

Potentiometric measurements were carried out with a Trüb and Täuber (Switzerland) compensation potentiometer. The indicator electrode was a platinum wire and the reference electrode was a saturated calomel electrode.

* Part III—see reference 4.

Colorimetric measurements were carried out with a colorimeter produced by Laboratorní potřeby, National Corporation, Prague.

POTENTIOMETRIC RESULTS

From a series of potentiometric titrations of cobalt^{II} with iron^{III} according to reaction (1) the influence of the concentration of bipyridyl and pH on this reaction was found.

To 5 ml of 0·01*M* cobalt^{II} nitrate solution were added 10 ml of a suitable buffer solution and a suitable amount of 0·01–0·1*M* bipyridyl solution. The solution was then diluted to 100 ml and titrated potentiometrically with 0·01*M* iron^{III} chloride solution.

The obtained results are in good agreement with the corresponding reaction

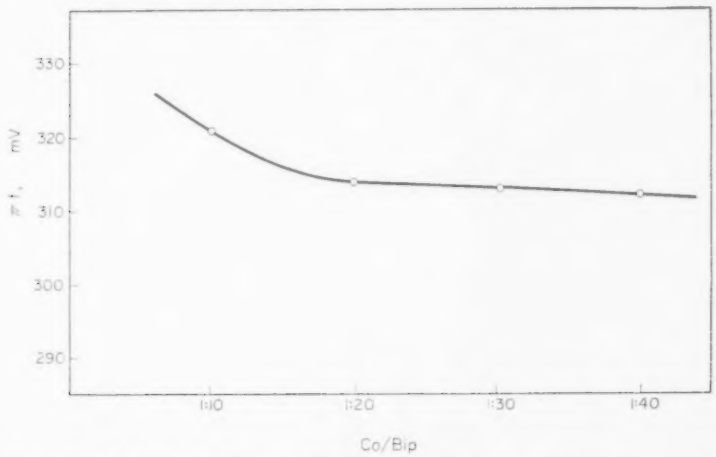

FIG. 1.—Influence of concentration of 2,2′-bipyridyl on the formal redox potential of the system:

$$Co(Bip)_3^{2+} \rightleftarrows Co(Bip)_3^{3+} + e$$
pH 3

which proceeds in the presence of 1,10-phenanthroline. The studied reaction was found to be a redox reaction with a one electron transfer and for the quantitative course of this reaction it is necessary to use a six-fold excess of 2,2′-bipyridyl. The optimal pH (from the point of view of the reaction velocity) was found in the range 2–4. The best buffer solution for this case is the mixture of monochloracetic acid and aqueous ammonia.

From the titration curves the formal redox potentials of the following redox systems were calculated:

$$Co(Bip)_3^{2+} \rightleftarrows Co(Bip)_3^{3+} + e \qquad (2)$$

$$(Fe^{II})_{Bip} \rightleftarrows (Fe^{III})_{Bip} + e \qquad (3)$$

The course of reaction (3) is not given here quite exactly, because the composition of the complex which is formed by reaction of the iron^{III} with 2,2′-bipyridyl was not studied. However, it would be expected that a similar hydroxo complex is formed to that in the case of 1,10-phenanthroline, $[Fe_2(OH)_2(Phen)_4]^{4+}$.

Paglia and Sironi[7] have found a formal potential of 0·31 V in chloride media for

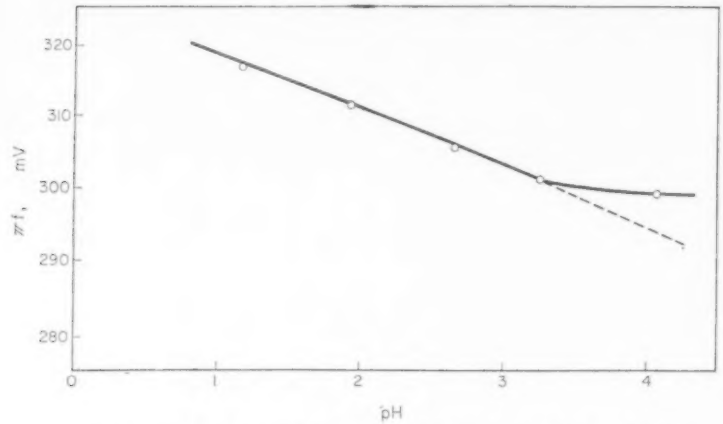

FIG. 2.—Influence of pH on the formal redox potential of the system:
$Co(Bip)_3^{2+} \rightleftarrows Co(Bip)_3^{3} + e$
ratio Co:Bip = 1:20.

redox system (2). We have found the same value at pH 2 in a buffer solution containing monochloracetic acid and ammonia. Under the same conditions we have found a value of 0·91 V for redox system (3).

The influence of the concentration of 2,2′-bipyridyl and pH (Figs. 1 and 2) on the formal redox potential of system (2) is very slight. This is because both oxidation states of cobalt have the same co-ordination number in the bipyridyl complex.[8]

In the case of system (3) the influence of the concentration of the complex forming reagent and pH on the formal redox potential is very great (Figs. 3 and 4). Here and similarly in the system with 1,10-phenanthroline, the influence of the concentration

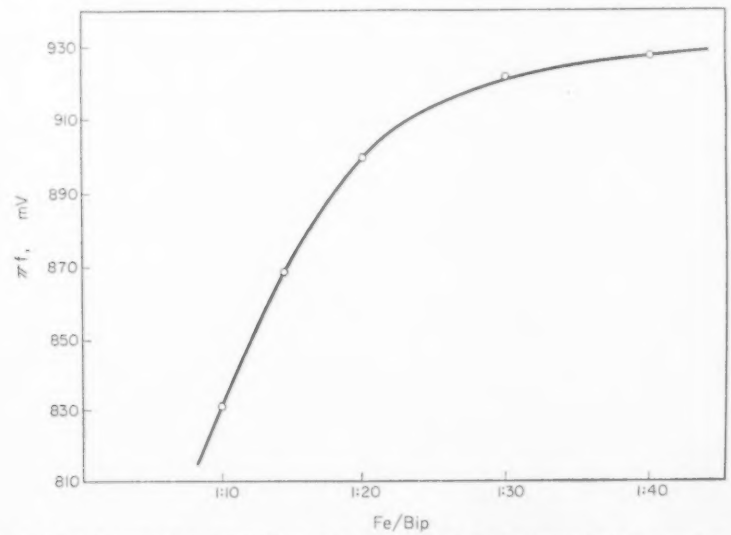

FIG. 3.—Influence of concentration of 2,2′-bipyridyl on the formal redox potential of the system:

$(Fe\ II)_{Bip} \rightleftarrows (Fe\ III)_{Bip} + e$
pH 3.

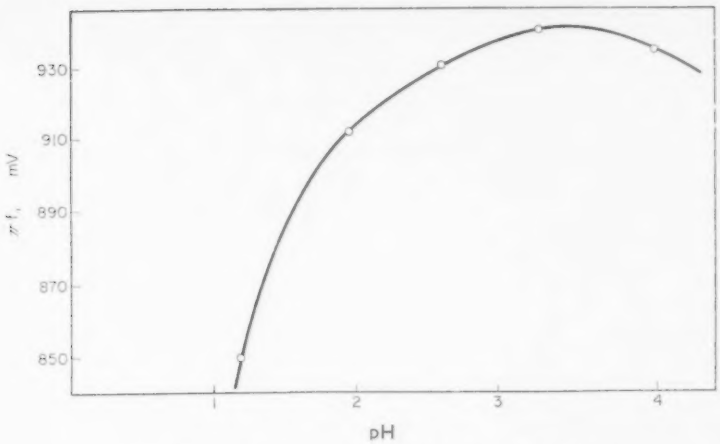

FIG. 4.—Influence of pH on the formal redox potential of the system:
$(Fe\ II)_{Bip} \rightleftarrows (Fe\ III)_{Bip} + e$
ratio Co:Bip = 1:20.

of the reagent is caused by the different values of the co-ordination number of iron in the complex in the two oxidation states.

COLORIMETRIC RESULTS

For the colorimetric study of reaction (1) the formation of the intensely coloured complex, $(Fe^{II})_{Bip}$ ($\lambda_{max} = 522$ mμ, $\varepsilon_{H_2O} = 8930$), which is formed by the reduction of iron^{III} with cobalt^{II} in the presence of 2,2′-bipyridyl has been used.

Under similar experimental conditions to those in the colorimetric study of the oxidation of cobalt^{II} with iron^{III} in the presence of 1,10-phenanthroline[2] identical results were found for the studied redox reaction. From the determination of the ratio of the reacting components it was stated that a one-electron transfer occurs during the reaction (ratio of Co:Bip = 1:1) and that its quantitative course needs a constant excess of 2,2′-bipyridyl [ratio (Co + Fe) : Bip = 1 : 6]. From these results it was confirmed that the composition of the resulting complexes was $Fe(Bip)_3^{2+}$ and $Co(Bip)_3^{3+}$. During the study of the influence of pH it was found that the quantitative course of this reaction takes 15 min in solutions of pH 1·5–5.

ANALYTICAL APPLICATIONS

The analytical utilisation of reaction (1) for the determination of cobalt is the same as the utilisation of the similar reaction with 1,10-phenanthroline. The difference in the values of the formal redox potentials of redox systems (2) and (3) is 0·60 V, and for the corresponding redox systems with 1,10-phenanthroline this difference is only 0·44 V. The potential change during the titration of cobalt^{II} with iron^{III} is greater in the presence of 2,2′-bipyridyl. The potential jump at the equivalence point is 450 mV per 0·05 ml of 0·01 *M* iron^{III} chloride solution. The velocity of the stabilisation of the potential is practically the same as in the case of using 1,10-phenanthroline.

During the indirect cerimetric titration of cobalt [oxidation of $Fe(Bip)_3^{2+}$, which is formed according to reaction (1)] good results were not obtained, probably because $Fe(Bip)_3^{3+}$ is not very stable in this medium. Similarly, for the indirect colorimetric determination of very small quantities of cobalt, it is better to use 1,10-phenanthroline

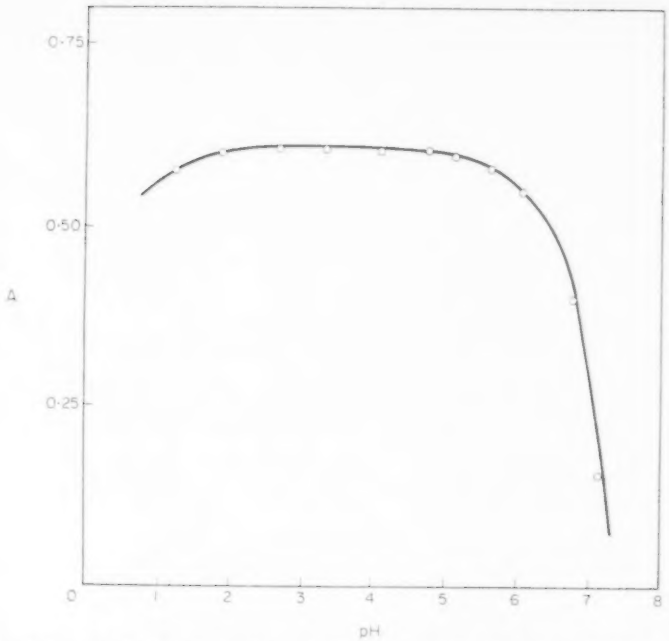

FIG. 5.—Influence of pH on extinction of $Fe(Bip)_3^{2+}$ resulting from the oxidation of cobalt^{II} with iron^{III} chloride solution. 2 ml of 0·001*M* $Co(NO_3)_2$, 5 ml of 0·001*M* $FeCl_3$, pH adjusted with 0·1*N* HCl or 0·1*N* NaOH (glass electrode) and 5 ml of 0·1*M* 2,2′-bipyridyl of the same pH, total volume of 25 ml. The extinction was measured after 15 min (1 cm cell, 522 mμ).

as the complex forming reagent,[5] because the intensity of the colour of ferroïn is higher ($\varepsilon_{H_2O} = 11\,100$) than the intensity of the similar complex of iron^{II} with 2,2′-bipyridyl.

Zusammenfassung—Die Oxydation von Cobalt(II) mit Eisen(III) in Gegenwart von 2,2-Dipyridyl wurde potentiometrisch und photometrisch studiert. Die Reaktion ist analog zu der früher mit Phenanthrolin studierten. Die Formalpotentiale der Reaktion wurden berechnet und ihre Anhängigkeit von Reagenzmenge und pH studiert. Die Anwendungsmöglichkeit des Redoxsystems zur Bestimmung von Cobalt wird diskutiert.

Résumé—Les auteurs ont étudié l'oxydation du cobalt(II) par le fer(III) en présence de 2,2-bipyridile par potentiométrie et colorimétrie. La marche de cette réaction correspond à celle dé la réaction d'oxydo-réduction étudiée antérieurement, ou la 1,10 phénanthroline était utilisée comme réactif formant le complexe. Les potentiels normaux apparents de la réaction ont été calculés et leurs variations en fonction de la concentration de 2,2-bipyridile et du pH ont été étudiées. Finalement, les auteurs discutent de la possibilité d'utiliser ce système oxydo-réducteur pour le dosage du cobalt.

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PRELIMINARY COMMUNICATIONS

Evaluation and correlation of partition parameters involved in paper chromatography*†

(*Received* 8 *May* 1961. *Accepted* 11 *June* 1961)

THE theoretical approach to partition chromatography developed by Martin and his co-workers[1,2] has received wide acceptance and has demonstrated considerable predictive and correlative value.[3–6] However, the inability to evaluate the partition parameters described by Martin and, hence, the failure to correlate them with experimental conditions has meant that the full utility of the theory could not be exploited. The details for evaluating the parameters and several ways in which the knowledge of these functions may be of some aid in selecting experimental conditions are described below.

A graphical procedure to evaluate the partition parameters involved in the mobility of a homologous series of compounds became possible after development of equations presented by Martin,[1] Consden *et al.*[2] and French and Wild[3] into the form:

$$\log_{10}\frac{R_{f_n}}{1-R_{f_n}} = \log_{10}\frac{A_m}{A_s} - 0.434\,\frac{\Delta\mu_y}{RT}\left(\frac{\Delta\mu_x}{\Delta\mu_y} + n - 1\right). \qquad (1)$$

where R_{f_n} is the R_f of an n-mer, A_m and A_s are the areas of the mobile phase and stationary phase,[2] respectively, $\Delta\mu_x$ and $\Delta\mu_y$ are, respectively, the free energy necessary to transfer a mole of monomer x and the added monomer unit y from the stationary phase to the mobile phase, and n is the chain length. Assuming that $\frac{A_m}{A_s}$ and $\frac{\Delta\mu_x}{\Delta\mu_y}$ are constants independent of solvent, the parametric equation (1) predicts that if $\log_{10}\frac{R_{f_n}}{1-R_{f_n}}$ is plotted *vs.* $n-1$ for various values of $\Delta\mu_y$, a family of lines should result, intersecting at the co-ordinate, $\log_{10}\frac{A_m}{A_s}$, $-\frac{\Delta\mu_x}{\Delta\mu_y}$, with slopes of $\frac{-0.434\Delta\mu_y}{RT}$. Furthermore, the intercept at $n-1=0$ will be $\log_{10}\frac{A_m}{A_s} - \frac{0.434\Delta\mu_x}{RT}$.

To test the veracity of the assumptions and the possibility that equation (1) could lead to a procedure for evaluating the partition parameters for homologues, the mobilities of the maltodextrin saccharides[7] were measured on Whatman No. 2 and Eaton and Dikeman No. 613 paper at 24° ± 1° (after equilibration with the solvent vapours) with various mixtures of water and *t*-BuOH (miscible in all proportions). Different solvent mixtures were used to produce various values of $\Delta\mu_y$. The results of the experiment are plotted in Fig. 1 on a semilogarithmic graph, and, as predicted, lines intersecting at a common point for a wide range of solvent proportions were found. At very high water concentrations (*cf.* upper curve, Fig. 1), the paper apparently begins to swell[8] excessively and the ratio, $\frac{A_m}{A_s}$, increases.

When the maltodextrins were chromatographed with ten different solvents on Eaton and Dikeman paper, it was learned that the ratio, $\frac{A_m}{A_s}$, was constant (2.65 ± 0.15) while the ratio, $\frac{\Delta\mu_x}{\Delta\mu_y}$, exhibited solvent dependence. The fact that $\frac{A_m}{A_s}$ for Eaton and Dikeman paper was significantly different from

* Contribution No. 1001 from the Chemical Laboratories of Indiana University.
† Research supported by a grant from Corn Industries Research Foundation.

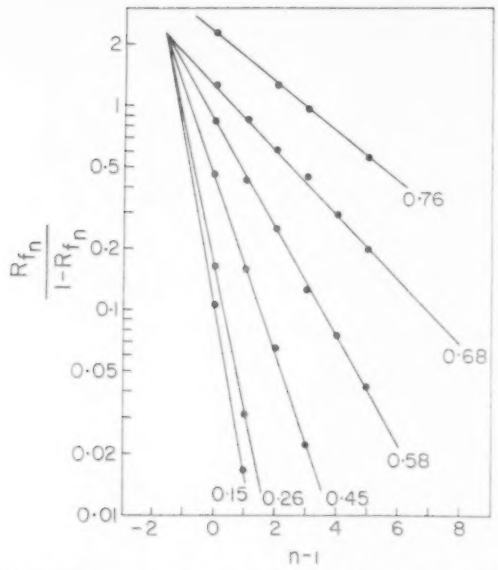

FIG. 1.—Mobility parameters of the maltodextrin saccharides *vs.* chain length minus one. Numbers correspond to mole fraction of water in the mobile phase containing *t*-BuOH as the organic component. Paper is Whatman No. 2.

the ratio of the areas obtained for Whatman No. 2 paper (2.10 ± 0.05) suggested that this function is primarily a property of the paper. Therefore, by studying the ratio, $\frac{A_m}{A_s}$, as a function of the paper, it should be possible to select the paper most suitable for individual chromatographic needs.

This treatment is not limited to homologous polymers, but can be extended to a general case which allows the parameters of any two similar compounds to be evaluated. Further manipulation of the basic equations leads to the following relationship for two compounds:

$$\log_{10}\frac{R_{f_a}}{1-R_{f_a}} = \log_{10}\frac{A_m}{A_s} + \left(\log_{10}\frac{R_{f_a}}{1-R_{f_a}} - \log_{10}\frac{R_{f_b}}{1-R_{f_b}}\right)\left(\frac{1}{1-\frac{\Delta\mu_b}{\Delta\mu_a}}\right), \qquad (2)$$

where R_{f_a} and R_{f_b} are the R_f of *a* and *b*, respectively, and $\Delta\mu_a$ and $\Delta\mu_b$ are respectively, the energies necessary to transport a mole of *a* and of *b* from the stationary phase to the mobile phase. Now if compounds *a* and *b* are similar in character so that $\frac{\Delta\mu_b}{\Delta\mu_a}$ is reasonably constant when solvent proportions in a given binary system are varied, then a plot of $\log_{10}\frac{R_{f_a}}{1-R_{f_a}}$ *vs.* $\log_{10}\frac{R_{f_a}}{1-R_{f_a}} - \log_{10}\frac{R_{f_b}}{1-R_{f_b}}$ will lead to a straight line with a slope of $\frac{1}{1-\frac{\Delta\mu_b}{\Delta\mu_a}}$ and an intercept of $\log_{10}\frac{A_m}{A_s}$.

The validity of equation (2) is verified by Fig. 2 where the appropriate plot is constructed for the two saccharides, glucose and maltose, which were studied in the water-*t*-BuOH system. Again, at high water concentrations the swelling of the paper becomes evident.

From thermodynamic considerations, after making a few simplifying assumptions, it can be shown that $\Delta\mu_a$ and hence $\log_{10}\frac{R_{f_a}}{1-R_{f_a}}$ (in the mixtures where $\frac{A_m}{A_s}$ is constant) would be linearly

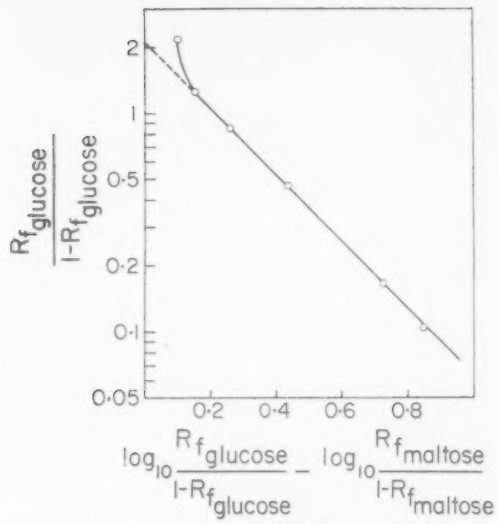

FIG. 2.—Mobility parameters of glucose *vs.* the difference in mobility parameters of glucose and maltose for various solvent proportions of water and *t*-BuOH. Paper is Whatman No. 2.

related to the mole fraction of water, N_{H_2O}, of a binary solvent. From the plot in Fig. 3, it can be seen that a linear relationship between $\log_{10}\frac{R_{f_a}}{1-R_{f_a}}$ (where *a* represents glucose) and N_{H_2O} does exist over most of the range of solvent proportions tested.

Although the ratio, $\frac{\Delta\mu_x}{\Delta\mu_y}$, is a variable function of the solvent composition, it is independent of solvent proportions. Since this free energy ratio is an objective index of the ability of a particular set of components to separate mixtures, it serves as an excellent guide in the selection of solvent components.

The developments presented here suggest a method for selecting the solvent proportions producing

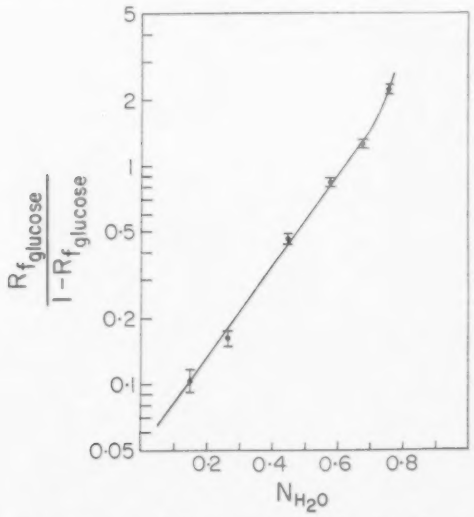

FIG. 3.—Mobility parameter of glucose *vs.* the mole fraction of water in the developing solvent. Paper is Whatman No. 2; organic solvent is *t*-BuOH.

maximum separation. From Fig. 2, for example, it is possible by graphical means to determine the R_f of glucose when maximum separation between glucose and maltose is achieved. From Fig. 3, the N_{H_2O} of the solvent producing this R_f for glucose or maximum separation is assessed. Although glucose and maltose are too easily separated to use this technique, it should be useful for the separation of compounds having more similar R_f values.

The evaluation of the influence of environmental factors such as solvent, paper, temperature, salts, *etc.* on the ratios of $\frac{A_m}{A_s}$ and $\frac{\Delta\mu_x}{\Delta\mu_y}$ should enhance our ability to predict and find better conditions for chromatography.

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Indianapolis, Indiana, U.S.A.

Summary—A graphical method has been developed on theoretical grounds for evaluating the partition parameters involved in the mobility of a homologous series of compounds undergoing partition chromatography. The method has been tested by applying it to maltodextrin saccharides. The method permits an assessment of the solvent proportions which would favour maximum separation.

Zusammenfassung—Ein graphische Methode wurde auf Grund theoretischer Erwägungen entwickelt um die Verteilungsparameter homologer Reihen von Verbindungen für gaschromatographische Zwecke zu berechnen. Das Verfahren wurde durch Anwendung auf Saccharide von Maltodextrin getestet. Die Methode gestattet eine Bewertung der Solventeigenschaften um die höchstmögliche Trennung zu erzielen.

Résumé—L'auteur a mis au point d'après des bases théoriques une méthode graphique pour évaluer les coefficients de partage mis en jeu pour une série homologue de composés dans la chromatographie de partage. La méthode a été expérimentée sur les saccharides maltodextrines. Elle permet une estimation des proportions de solvant favorisant une séparation maximale.

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Applications of infra-red spectroscopy—VI*

Recent developments in techniques of increased sensitivity for the analysis of GLC fractions and other small scale samples—a brief review

(*Received* 23 *August* 1961. *Accepted* 30 *August* 1961)

THE relative cost of acquiring the appropriate apparatus has probably contributed significantly to the unfortunate fact that, of absorption spectroscopic methods, colorimetry and ultraviolet have been more frequently applied to analytical problems than infrared. Recently, however, the availability of

* Part V: D. M. W. Anderson and N. J. King, *Talanta*, 1961, **8,** 497.

less expensive equipment has fostered greatly increased interest in the analytical uses of infrared spectroscopy. The emphasis, however, has been on qualitative applications; the tremendous potential which infrared offers to quantitative analysis does not appear to have been adequately appreciated. Infrared not only identifies unequivocally, but simultaneously gives a basis for accurate quantitative analysis if the appropriate calibration curves on standards are constructed. Moreover, the sample is not destroyed, and the nature of any contaminants is revealed. Generally, contaminants rarely interfere with quantitative determination of the desired compound if the operating conditions are carefully chosen, but if interference does occur, adequate warning is given by the appearance of the spectrum. The literature continues to describe analytical procedures which could be carried out more rapidly and accurately, with decreased interference from other components, by infrared methods.

General interest in the analysis of smaller and smaller amounts of material continues, and has naturally stimulated efforts to increase the sensitivity of all spectroscopic techniques. For infrared this can be approached by the use of auxiliary instrumentation such as scale-expansion,[1] multipathlength cells,[2] or beam condensers—all of which are relatively expensive—or by improving the design of single-pass cells. Techniques are now clearly established[3] for the quantitative analysis of 20–100 μg of material in solution or in the liquid, solid, or gas phase; various techniques and accessories permitting the examination of <1 μl of some samples have also been described[4] or commercially advertised.

The greatest stimulus to the development of increased sensitivity has doubtless come from the challenge for spectroscopists to approach the sensitivity attainable in chromatographic separations. This challenge has been invaluable, since the resulting spectroscopic developments are equally applicable to samples which are not of chromatographic origin. Throughout the development of both techniques, samples obtained as GLC fractions have always tested the minimum limits detectable by infrared; it now appears that spectroscopic techniques may never match the chromatographic sensitivity attained recently through the development of capillary columns.

Indeed, some authorities[5] consider that the identification of GLC fractions may have to be based solely on the use of retention-volume characteristics. Although this is doubtless satisfactory for routine applications, its serious deficiencies when applied to entirely unknown mixtures from research investigations, or to systems which have not been completely characterised, have already received comment.[6] A triangulation method using three stationary phases of differing polarities has been proposed[7] for the positive identification of GLC components, but many investigators are agreed[4,6,8–10] that identification based solely on retention characteristics is inadequate. Compounds can have closely similar retention volumes, even on different column materials; components may only be separable[9] as "shoulders"; and mixtures of similar hydrocarbons[10] or of members of different homologous series[8] may be found under a single chromatographic peak. The collection of fractions and subsequent examination by infrared[4,6,11] or mass spectroscopy[9,10] is therefore desirable; continuous infrared detection of functional groups has also been proposed.[12] If spectroscopic equipment is not available, then functional group analysis[8,13] of the eluted fractions is desirable, and can be operated at the 20-μg level.

Considering now only infrared techniques, it is clear that the dominant difficulty lies in matching the sensitivity of GLC. When co-operation between the two techniques is essential, a possible solution is to operate below maximum GLC sensitivity; this, however, could only be taken a certain length before leading to column overloading or to decreased chromatographic resolution. All too frequently, the particular component to be studied is present in trace amount in a mixture: even although an adequate supply of the mixture is available, insufficient amounts of the required fraction for infrared examination may be given by each chromatographic fractionation. It appears, therefore, that there will always be a demand for the technique of trapping the appropriate peak from a number of consecutive GLC runs, so that eventually a quantity sufficient for spectroscopic identification is collected.[6] Techniques involving collection in liquid nitrogen traps are now frequently used.[4,14] Other methods, such as mixing the eluted fraction with a vapour solvent introduced *via* a side-arm to the trap,[15] or depositing the desired component at room temperature on finely ground potassium bromide, which is subsequently pressed to form a disc,[16] have also been described.

Although it has clear limitations[6] (*cf.* ref. 4), the vapour-phase technique remains invaluable for certain types of sample, and any increase in its sensitivity[11] would be advantageous. Although metal cells of uniform rectangular cross-section[4] can increase the sensitivity given by circular glass-cells,[11] they do not, however, give the maximum sensitivity attainable with single-pass cells. Metal cells having

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tapered bores of rectangular cross-section, such that all essential rays of the energy beam are exactly enclosed, became available commercially for certain spectrometers during 1960: tapered cells made here for use with the Hilger H800 instrument were shown to visitors to this department during the 3rd International Gas Chromatography Symposium. It is of interest that the asymmetrically placed focus of the H800 spectrometer gives some advantage in designing such a tapered cell for insertion in the energy beam between the point of focus and the spectrometer entrance slit, rather than (*a*) between the energy source and the point of focus or (*b*) symmetrically about the focus.

That such rectangular tapered cells are more conveniently constructed of metal rather than of glass introduces no disadvantages; the examination of corrosive or reactive compounds merely requires the surfaces of the cell to be thinly covered with an epoxy or other coating suitably inert to the compound being examined. Indeed there now appears to be a distinct advantage in also constructing the trap and stop-cocks of metal; when trap dimensions are reduced, the increasing fragility of glass is off-set. A trapping device employing hypodermic needle tubing has been described.[17]

Suitably small vacuum-tight metal stop-cocks are now available commercially; these facilitate all-metal construction, although there is no difficulty in incorporating glass stop-cocks[4] in an otherwise metal assembly. It has long been known, however, that the presence of stop-cock grease is undesirable.[18] The importance of using minimal amounts of lubricants was stressed earlier,[6] but in working with ever decreasing amounts of material, there are now distinct indications that *all* traces of lubricants must be eliminated. High-vac greaseless taps are now offered commercially, and greaseless laboratory devices have been described.[18,19]

The future development of minimum volume, all-metal, greaseless trap-cells may also simultaneously assist the incorporation of heating devices so that the applicability of the vapour-phase technique may be extended above its present limit of about 125° (*cf.* refs. 4 and 11). Development of heated cells[6] suitable for accurate quantitative work has proved troublesome; difficulty has also been reported by other investigators.[4] Nevertheless a vapour cell operating at ±1° up to 180° has been developed.[20] The results of continued efforts in this laboratory will be published in due course.

Finally, the development of new infrared transmitting glass such as "Irtran-2" (Eastman-Kodak Ltd.) which gives >70% transmission from 2-10 μ, decreasing to 40% at 14 μ, and which has good thermal shock properties, may facilitate the development of a single unit trap-cell which could be cooled directly to trapping temperature, then heated to volatilise the sample. Such cells may also be suitable for aqueous systems. The technique of trapping directly in evacuated gas-cells has recently been used.[14]

Acknowledgement—I am grateful to Dr. W. Zehden (Messrs. Hilger and Watts) for helpful discussions, in November last year, regarding the design of single-pass gas-cells of maximum sensitivity for use in Hilger H800 spectrophotometers.

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Summary—The advantages of quantitative infrared spectroscopy recommend the technique for wider application to analytical procedures than at present. Micro-scale samples can already be dealt with, and recent developments leading to increased sensitivity are briefly reviewed, with particular reference to the examination of samples in the vapour phase.

Zusammenfassung—Die sehr Vorteilhafte quantitativer IR-Spectroskopie wird zur ausgedehnteren Anwendung empfohlen. Es ist bereits möglich mit Mikroproben zu arbeiten; jüngste Entwicklungen führten zu erhöhter Empfindlichkeit, was im Hinblick auf die Untersuchung von Proben in der Dampfphase behandelt wird.

Résumé—L'auteur recommande les avantages de la spectroscopie infrarouge quantitative pour une application plus importante aux méthodes analytiques. Des échantillons miscroscopiques peuvent déjà être traités; les développements récents conduisant à une sensibilité accrue sont brièvement passés en revue, avec une référence particulière pour l'étude des échantillons en phase vapeur.

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Talanta, 1961, Vol. 8, p. 836. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEW

Gas Sampling and Chemical Analysis in Combustion Processes. G. TINÉ. AGARDograph 47, Pergamon Press, 1961. pp. 94. Price 42s.

THE extent of current interest in the chemistry of combustion is reflected in the large number of papers on this subject appearing in the literature. The scope of this interest extends from the purely practical aspects, such as estimations of fuel efficiency and engine performance, to the theoretical interpretation of reaction mechanisms. One problem is common to all of these studies and that is the analysis of reactant and burned gases. Without reliable methods of estimating the composition of gas mixtures no progress would be possible in the field of combustion, and it is, therefore, surprising that up till now no compilation of suitable analytical techniques has appeared. In writing *Gas Sampling and Chemical Analysis in Combustion Processes*, the author has attempted to fill this gap and, to a limited extent, he has succeeded.

The book is essentially a brief review of current methods used in the sampling and analysis of combustion gases. The information contained in it has been collected by the author, during a tour of industrial and university laboratories in countries associated with AGARD and, on the whole, the emphasis is more on the industrial approach than on the academic.

There are two main sections, the first dealing with sampling procedures and the second with gas analysis. The first section contains a brief theoretical discussion of the hydrodynamic problems associated with probe sampling. This is followed by theoretical and practical considerations of probe design and the techniques involved in sample handling and storage. In any analytical method which uses probe sampling, there are two important factors which must always be considered; they are the quenching effect, and possible catalytic effects arising from the probe. Both of these subjects are discussed, the first in considerable detail. It is to be regretted, however, that the second is given relatively little attention.

The second section begins with a review of basic analytical procedures in gas analysis and then deals with the recognised methods of analysis for the main components of a combustion mixture. All of the common components, likely to be encountered in practice, are reviewed, *e.g.*, H_2, O_2, H_2O, CO, CO_2, oxides of sulphur, alcohols, ethers, aldehydes and organic peroxides. A similar section follows this, on the analysis of exhaust gases. Emphasis is laid on modern instrumental techniques, such as gas chromatography, infrared spectral analysis and mass spectrometry. Each section is followed by a brief summary and recommendations.

The book is attractively presented and makes good use of diagrams in all cases where they are necessary. Constructive criticism of the various sampling and analytical procedures is provided throughout, together with references to original papers. It is, however, by no means a comprehensive text on the subject. The compilation of references could profitably be larger and a more detailed description of some of the techniques would have been valuable. Nevertheless, workers in the field of combustion will find this book useful introductory reading and a good guide to recent developments in gas analysis.

W. D. MCGRATH

Talanta, 1961, Vol. 8, pp. 837 to 838. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

UNITED KINGDOM

Friday 1 *December* 1961: **The Design and Construction of Laboratories:** Mr. R. R. YOUNG, F.R.I.B.A. and Mr. P. J. HARRINGTON: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, Manchester Section.* Manchester Literary and Philosophical Society, 36 George Street, Manchester, 1. 2.00 p.m.

This meeting will be preceded by a visit to I.C.I., Pharmaceuticals Division, Alderley Park, Cheshire. The party will leave central Manchester at 9.00 a.m.

Thursday 7 *December* 1961: **The Ramsay Dinner:** *Society for Analytical Chemistry, Scottish Section.* Central Hotel, Glasgow. 7.00 p.m.

Friday 8 *December*, 1961: **The Structure of Natural Products by Direct X-ray Analysis:** Professor J. MONTEATH ROBERTSON, D.Sc., F.R.S.: *Society for Analytical Chemistry, Scottish Section; Chemical Society; Society for Chemical Industry, Glasgow Section* and *Royal Institute of Chemistry, West of Scotland Section.* Royal College of Science and Technology, George Street, Glasgow. 7.15 p.m.

Friday 8 *December* 1961: **Analytical Research:** Dr. J. HASLAM, D.Sc., F.R.I.C.: *Society for Analytical Chemistry, Western Section* and *Royal Institute of Chemistry, Cardiff and District Section.* University College, Cardiff.

Wednesday 13 *December* 1961: **Fluorescent Indicators for Metals:** Dr. W. I. STEPHEN: *Society for Analytical Chemistry, Midlands Section.* University, Edgbaston, Birmingham, 15. 7.00 p.m.

Wednesday 13 *December* 1961: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 14 *December* 1961: **Annual General Meeting** followed by discussion on **Assessment of Antiatherosclerotics:** *Society for Analytical Chemistry, Biological Methods Group. The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

Friday 15 *December* 1961: **Applications of Infrared Spectroscopy to Quantitative Analysis:** *Society for Analytical Chemistry* and *Infrared Discussion Group.* King's College, Strand, London, W.C.2. 11.15 a.m.

First Session

Introductory Paper on Principles of Quantitative Infrared Spectroscopy: Dr. W. R. WARD
Quantitative Infrared Analysis of Agricultural Chemicals: Mr. P. G. MARSHALL

Second Session

Quantitative Analysis of Milk and other Emulsions by Infrared Absorption: Dr. J. D. S. GOULDEN
Quantitative Infrared Analysis of Phosphonitrilic Chloride Polymers: Dr. A. C. CHAPMAN
Some Uses of Infrared Spectroscopy in the Pharmaceutical Industry: Dr. H. D. C. RAPSON

The following Amendment Slips are announced by *B.S.I. News:*

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 16: 1961: *Reporting of results. Amendment No. 1: PD* 4254.

B.S. 1121: *Methods for the analysis of iron and steel: Part* 34: 1955: *Determination of molybdenum in iron and steel (absorptiometric method). Amendment No. 1: PD* 4149.

B.S. 2690: 1956: *Methods of testing water used in industry. Amendment No. 1: PD* 4220.

B.S. 2782: *Methods of testing plastics: Part* 4: 1958: *Analytical methods and viscosity in solution. Amendment No.* 6: *PD* 4291.

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys: Part* 3: 1961: *Antimony in ingot (photometric method). Amendment No. 1: PD* 4286.

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UNITED STATES OF AMERICA

Thursday-Saturday 7–9 *December* 1961: **Combined Southwest-Southeast Regional American Chemical Society Meeting.** New Orleans, Louisiana.

The tentative programme schedule lists 36 half-day sessions (23 general sessions and 13 symposia). All except the Biochemistry sessions will be held in the Jung Hotel. The final convention programme, containing abstracts of all papers to be presented, will be available at the time of registration.

The tentative programme for the Analytical Chemistry sessions is as follows:

Thursday Morning, 7 *December*

Paper Chromatography of Urethian Derivatives of Alcohols: JOHN A. ATTAWAY.

Spectrophotometric Determination of Zinc in Oilfield Brines: A. GENE COLLINS and TOM G. EBREY.

Kinetics of Extraction of Zinc Dithizonate: CARL B. HONAKER and HENRY FREISER.

Radiochemical Determination of Yttrium and Promethium—A Precipitation Technique: M. E. PRUITT, R. R. RICKARD and E. I. WYATT.

Simultaneous Differential Thermal Analysis and Gas Evolution Analysis—A New Technique: WESLEY W. WENDLANDT.

O-Dialkyl Phosphorodithionates as Extractants for Metals: THOMAS H. HANDLEY and JOHN A. DEAN.

Simultaneous Spectrophotometric Determination of Platinum and Palladium with Dibenzyldithiooxamide: WILLIAM D. JACOBS.

Gravimetric Determination of Indium by Benzenephosphonic Acid: ANIL K. MUKHERJI.

Thursday Afternoon, 7 *December:* **Symposium on Electroanalytical Chemistry**

Faradaic Rectification: PAUL DELAHAY.

Mechanisms of Electroreductions of Organic Compounds and Methods for their Elucidation: W. H. REINMUTH.

Electrochemistry of Adsorbed Reactants: F. C. ANSON.

Friday Morning, 8 *December:* **Symposium on Electroanalytical Chemistry.**

The Application of Controlled Potential Coulometry to the Study of Electrode Mechanisms: A. J. BARD.

Reactions at the Hanging Drop Mercury Electrode: IRVING SHAIN.

Friday Afternoon, 8 *December*

The Anodic Oxidation of Methyl and Ethyl Alcohols at Platinum Electrodes using Triangular Impulse Polarography: THOMAS C. FRANKLIN and CHARLES LIANG.

Current-Scan Polarography using a System which Ordinarily Exhibits a Polarographic Maximum: HARRY B. MARK, JR. and CHARLES N. REILLEY.

Current Programming in Chronopotentiometry: ROYCE W. MURRY.

A New Potentiometric Reaction Method for the Micro Determination of Carbonyl Compounds: H. V. MALMSTADT and E. C. TOREM, JR.

Amperometric Titrations with Ethylenedinitrilotetra-acetic Acid using Iron^{II} as the Indication Ion: G. GOLDSTEIN, D. L. MANNING and H. E. ZITTEL.

Exchange of Copper^{II} between EDTA and Eriochrome Blue Black R: D. W. RODGERS, D. A. AIKENS and C. N. REILLEY.

Saturday Morning, 9 *December*

Precipitation of Cobalt 8-Hydroxyquinolate from Homogeneous Solution: ROBERT W. SHERRILL.

Flame Spectrophotometric Determination of Trace Quantities of Strontium in Macro Quantities of Calcium: T. C. RAINS, H. E. ZITTEL and MARIAN FERGUSON.

Extraction of Sulphides from Petroleum Fractions by Way of Sulphonium Salts: R. L. HOPKINS, H. J. COLEMAN, C. J. THOMPSON and H. T. RALL.

Spectrographic Analysis of the Parts of a High-Lithium Rabbit: CHARLES H. SMITH.

The Extraction of Rhenium with Tributylphosphate: G. W. LEDDICOTE and A. P. GRIMANIS.

The Determination of Stable Trace Elements in Radioactive Materials by Neutron Radioactivation Analysis: W. T. MULLINS, F. F. DYER, J. F. EMERY, L. C. BATE and G. W. LEDDICOTE.

The Estimation of Beryllium with Eriochrome Cyanine R using the Ring Oven Technique: PHILLIP W. WEST and PATRICIA R. MOHILNER.

Further details may be obtained from the Publicity Chairman: P. D. ACCARDO, California Chemical Co., Oronite Division, Belle Chasse, Louisiana, U.S.A.

Talanta, 1961, Vol. 8, pp. 839 to 840. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Photometric titrations-VI: The determination of submicrogram quantities of calcium and magnesium: H. FLASCHKA and P. SAWYER. (10 *August* 1961).

Chelometric titrations with amperometric end-point detection: R. T. CAMPBELL and CHARLES N. REILLEY. (11 *September* 1961).

Precipitation of copper salicylaldoximate from homogeneous solution: RICHARD F. PIETRZAK and LOUIS GORDON. (22 *September* 1961).

Infrared spectra of some organophosphorus extractants: L. C. THOMAS and ROSEMARY A. CHITTENDEN. (29 *September* 1961).

The coulometry and polarography of iridium[IV]: JOHN A. PAGE. (2 *October* 1961).

PUBLICATIONS RECEIVED

Vol. 8 1961

The Radiochemistry of Vanadium: J. L. BROWNLEE, JR. NAS-NS-3022. National Academy of Sciences, National Research Council. December, 1960. Pp. v + 76. $0.75.

The Radiochemistry of Ruthenium: E. I. WYATT and R. R. RICKARD. NAS-NS-3029. National Academy of Sciences, National Research Council. February, 1961. Pp. vii + 78. $1.00.

The Radiochemistry of Selenium: G. W. LEDDICOTTE. NAS-NS-3030. National Academy of Sciences, National Research Council. April, 1961. Pp. v + 38. $0.50.

The Radiochemistry of the Transcurium Elements: G. H. HIGGINS. NAS-NS-3031. National Academy of Sciences, National Research Council. Pp. v + 34. $0.50.

The Radiochemistry of Aluminum and Gallium: JOHN E. LEWIS. NAS-NS-3032. National Academy of Sciences, National Research Council. April, 1961. Pp. v + 48. $0.50.

The Radiochemistry of Antimony: WILLIAM J. MAECK. NAS-NS-3033. National Academy of Sciences, National Research Council. February, 1961. Pp. vi + 54. $0.50.

The Radiochemistry of Titanium: CHONG KUK KIM. NAS-NS-3034. National Academy of Sciences, National Research Council. March, 1961. Pp. v + 23. $0.50.

The Radiochemistry of Cesium: H. L. FINSTON and M. T. KINSLEY. NAS-NS-3035. National Academy of Sciences, National Research Council. Pp. vi + 68. February, 1961. $0.75.

Radioactive Contamination of Materials Used in Scientific Research: JAMES R. DEVOE. Publication 895. National Academy of Sciences, National Research Council. 1961. Pp. vii + 142.

Chromatography with particular consideration of Paper Chromatography: E. MERCK A.G. Verlag Chemie, Weinheim, 1961. Pp. 185. 2nd Edition. DM.18-.

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Gas Sampling and Chemical Analysis in Combustion Processes: G. TINE. Pergamon Press Limited, Oxford, 1961. Pp. 94. 42s.

The Radiochemistry of Gold: J. F. EMERY and G. W. LEDDICOTTE. NAS-NS-3036. National Academy of Sciences, National Research Council. May, 1961. Pp. v + 34. $0.50.

Liquid-Liquid Extraction with High-molecular-weight Amines: FLETCHER L. MOORE. National Academy of Sciences, National Research Council. 15 December, 1960. Pp. v + 83. $1.00.

Principles and Applications of Paper Electrophoresis: CH. WUNDERLY. Elsevier. 1961. Pp. xii + 253. 26s.

Advances in Fluorine Chemistry—II: Editors: M. STACEY, J. C. TATLOW and A. G. SHARPE. Butterworths. 1961. Pp. 220. 45s.

Encyclopaedic Dictionary of Physics: Pergamon Press Limited, Oxford, 1961. Vol. I, Pp. xv + 800. £80 per set.

The Encyclopedia of Microscopy: Edited by GEORGE L. CLARKE. Chapman and Hall. 1961. Pp. xiii + 693. 200s.

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Systematic Qualitative Analysis: G. A. MORRISON. Butterworths. 1961. pp. ix + 198. 25s.

Rules and Methods for Calculating the Physico-Chemical Properties of Paraffinic Hydrocarbons: V. M. TATEVSKII, V. A. BENDERSKII and S. S. YAROVOI. Pergamon Press Limited, Oxford, 1961. pp. xi + 128. 30s.

Radiochemistry: Pergamon Press Limited, Oxford, 1961. Vol. I, No. I, pp. 183. £15 p.a.

Separations by Solvent Extraction with Tri-n-octylphosphine Oxide: J. C. WHITE and W. J. ROSS. NAS-NS-3102. National Academy of Sciences, National Research Council. 8th February, 1961. pp. v + 56. $0.75.

Low-level Radiochemical Separations: T. T. SUGIHARA. NAS-NS-3103. National Academy of Sciences, National Research Council. April, 1961. pp. v + 34. $0.50.

A Cross-referenced Index of Radiochemical Teaching Experiments Applicable to Chemistry: GREGORY R. CHOPPIN. Publication 905. National Academy of Sciences, National Research Council. 1961. pp. 50. $1.00.

Quantitative Organic Microanalysis: AL STEYERMARK. 2nd Edition. Academic Press, 1961. pp. xvii + 665. 118s.

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The Radiochemistry of Tellurium: G. W. LEDDICOTTE. NAS-NS-3038. National Academy of Sciences, National Research Council. July, 1961. pp. v + 42. $0.50.

Methods for the Analysis of Non-Soapy Detergent (NSD) Products: G. F. LONGMAN and J. HILTON. Society for Analytical Chemistry, 1961. pp. 30. 15s.

A Guidebook to Mechanism in Organic Chemistry: P. SYKES. Longmans, Green and Co. Ltd., 1961. pp. xiii + 247. 21s.

Separation of Heavy Metals: ANIL K. DE. Pergamon Press Limited, Oxford, 1961. pp. 308. 60s.

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BEITRÄGE ZUM AUFBAU EINIGER METALL-CARBAMATVERBINDUNGEN

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(*Received* 15 *March* 1961. *Accepted* 23 *April* 1961)

Zusammenfassung—Es werden von einigen Metall-Carbamatverbindungen die Bruttoformeln, der Kristallhabitus und die entsprechenden Debye-Scherrer-Diagramme gezeigt.

UM den Aufbau einiger der immer stärker in den Vordergrund der analytischen Chemie tretenden Metall-Carbamatverbindungen näher kennenzulernen, wurden aus reinen Metallsalzlösungen in den günstigsten pH-Bereichen[1–4] die entsprechenden metallorganischen Fällungen hergestellt.

Im folgenden wird eine Aufstellung über die chemische Zusammensetzung, wie sie auf Grund von Elementaranalysen gefunden wurde, über den Kristallhabitus, wie er nach langsamer Kristallisation aus den Chloroformlösungen der entsprechenden Verbindungen entstand, und über die Röntgenfeinstruktur dieser auskristallisierten Verbindungen gebracht.

Bei den hier vorliegenden Untersuchungen wurden nur Pulverdiagramme aufgenommen unter Verwendung einer Debye-Scherrer-Kammer mit einem Radius von 28,65 mm. Als Strahlung diente Kobalt-Kα-Strahlung unter Vorschalten eines Eisenfilters. Die Aufnahme erfolgte symmetrisch zum einfallenden Strahl. Da keine Eichsubstanz mit aufgenommen wurde, sind die errechneten Netzebenenabstände nicht korrigiert. Die Aufspaltung in die Linien der Kα_1- und Kα_2-Strahlung wurde nicht beobachtet. Die Berechnung konnte daher mit der Wellenlänge Kα = 1,786 kXE durchgeführt werden. Die Intensität der Linien wurde geschätzt, wobei die stärkste Interferenzlinie jeder Aufnahme mit "sehr, sehr stark" bezeichnet wurde. Die *Tafel I* gibt die Netzebenenabstände der reinen Fällungsmittel, *Tafel II* die Netzebenenabstände einiger aus Chloroform umkristallisierter Diäthyldithiocarbamate und *Tafel III* die einiger ebenfalls aus Chloroform umkristallisierter Pyrrolidindithiocarbamate wieder. In den Tafeln sind die Interferenzlinien nicht nach fallendem Netzebenenabstand, sondern nach der Intensität geordnet. Es zeigt sich, daß alle Carbamate ein mehr oder weniger linienreiches Interferenzmuster ergeben und dass auch die Debye-Scherrer-Diagramme der Metallsalze sich untereinander sowie von den Fällungsmitteln unterscheiden. Die Kristallstruktur des Zinkdiäthyldithiocarbamates wurde eingehend von Simonsen und Wah Ho[5] untersucht.* Das vorliegende Debye-Scherrer-Diagramm stimmt im wesentlichen hinsichtlich der Intensitätsverteilung und Linienanzahl mit dem von den beiden vorher genannten Forschern

* Die aus Chloroform erhaltenen durchsichtigen. Plättchen sind optisch einachsig negativ. Die Struktur analyse ergab, daß es sich hier um eine monoklin kristallisierende Verbindung handelt mit

$a = 10{,}02 \pm 0{,}02$;
$b = 10{,}80 \pm 0{,}05$;
$c = 16{,}00 \pm 0{,}02$ Å
$\beta = 111.$

Die Raumgruppe hat 4 Elementarzellen.

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TAFEL I. NETZEBENENABSTÄNDE DER REINEN FALLUNGSMITTEL

Intensität geschätzt	Natriumdiäthyl-dithiocarbamat	Ammoniumdiäthyl-dithiocarbamat	Natriumpyrrolidin-dithiocarbamat	Ammonium-pyrrolidin-dithiocarbamat
	d kXE	d kXE	d kXE	d kXE
ststst	5,60 5,10	6,23	4,93 4,16	5,20 3,41
stst	4,21 2,71	6,58 4,24 4,08		2,82
st	3,40 3,19 2,93	7,58 5,20 5,00 3,23 3,14	3,27 3,11	7,83 3,89 3,20
m	2,44 1,89	4,66 4,45 3,68 3,56 2,81 2,74	3,89 2,53 2,21	5,60 4,17 2,86
s	3,07 2,10 1,79	3,42 3,05 2,96 2,50 2,45 2,20	3,60 3,42 2,45	3,62
ss	3,90 2,83 2,21 1,99	2,14 2,04 1,88 1,66	2,95 2,38 2,29 1,87 1,79	4,66 2,60 2,51 2,44
sss	2,59 2,05 1,67 1,41 1,40 1,35 1,33 1,30 1,28 1,23	3,90 2,88 2,29	2,09 2,01 1,97 1,72	2,36 2,20 1,92

ststst = sehr sehr stark
stst = sehr stark
st = stark
m = mittel
s = schwach
ss = sehr schwach
sss = sehr sehr schwach

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TAFEL II. NETZEBENENABSTÄNDE EINIGER METALLDIÄTHYLDITHIOCARBAMATE

Intensität	Ag	Cu	Zn	Cr	Mn	Fe	U
ststst	8,14	4,05 3,61	7,03	7,77	6,34	8,48 7,62	7,51 4,39
stst		8,20 5,88	9,07 8,27 5,88	4,38	4,13	6,67 6,08 3,96	
stst	9,07	9,09 3,02 2,59	4,34 4,14 3,73	3,48	5,10 2,47	4,22	
m	4,32 3,27 2,26	7,20 6,82 4,42 4,23 2,76 2,26	3,58 3,08 2,78 2,05	4,98	3,56 3,16 2,75	2,75	5,77 5,20 2,82 2,52
s	4,88 3,37 3,12 3,01 2,89 2,42 2,01	4,69 2,03 1,99 1,77 1,75	4,94 4,71 4,51 2,86 2,64 2,33 2,27 1,74	6,91	4,51 3,44	5,00 3,27 3,12	3,40 3,90 2,64 2,25
ss		2,31 2,21 2,16 1,92 1,88 1,83 1,66 1,59 1,53 1,47				2,16 1,89	
sss	3,76 2,79 2,71 2,48 1,97 1,83 1,80 0,76 1,71	3,75 2,69 2,10 1,80 1,70	2,94 2,13 1,86 1,69 1,51	4,63 4,05 3,76	5,50 1,98 2,01 1,71 1,58 1,54 1,43	5,40 4,50 3,68 2,99 2,55 1,91 1,67 1,59	6,26 2,43 2,33 2,18 2,04 1,92

ststst = sehr sehr stark
stst = sehr stark
st = stark
m = mittel
s = schwach
ss = sehr schwach
sss = sehr sehr schwach

TAFEL III. NETZEBENENABSTÄNDE EINIGER METALLPYRROLIDINDITHIOCARBAMATE

Intensität	Cu	Zn	Cd	Ni	Bi	Mn	Fe	Mo	Nb
ststst	3,58	7,56 4,18	9,32	7,13	9,44	4,53	4,68		7,30
stst	7,23 5,20 3,76			7,79 5,30 4,06	4,77 3,77		7,08	3,83	6,73
st	7,86 5,70	5,71 5,20 3,69 3,75	7,60 4,61 3,20	3,66	7,83 5,20	4,17	7,89 5,00 3,52	7,23	4,16
m	3,96 2,21 1,99	4,57 3,20	6,04 4,04 2,77 2,36	3,51	2,88 2,61	2,78	6,11 4,30 4,00 3,24 3,10 2,66 2,39	6,75 3,44	5,30 3,41
s	2,82 2,74 2,44 2,29	2,64 2,48 2,34 2,12 1,98	3,78 3,29 2,15 1,98	5,60 4,28 3,28	7,20 5,82 3,09 2,73 2,39 2,33		3,84 3,69 2,58 2,47 1,98 1,92	5,60	4,89 2,16
ss	4,54 2,50 2,04 1,94 1,86 1,82 1,76 1,62 1,58	3,55 3,02 2,89 2,75 2,25 2,19 1,81 1,75	2,26 2,02 1,90	3,78 2,72 2,58 2,35 2,19 1,81	3,29 2,49 2,27 1,97 1,78 1,63	3,42	5,40 2,78 2,29 2,10 2,06 1,81 1,75 1,69	5,30 4,53	3,74 2,08 2,00 1,92
sss	4,14 3,05 2,90 2,35 2,08 1,79 1,73 1,69 1,66	6,42 4,89 3,35 1,92	5,00 2,47 2,06 1,61	6,25 4,51 3,45 3,03 1,97	3,46 2,11 1,91 1,55	3,87	2,92 2,19 2,14	4,04 3,24	2,73 2,38 2,30

ststst = sehr sehr stark
stst = sehr stark
st = stark
m = mittel
s = schwach
ss = sehr schwach
sss = sehr sehr schwach

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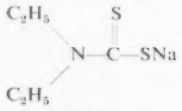
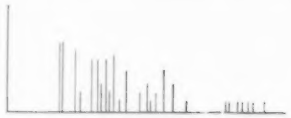
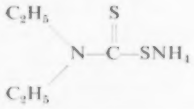
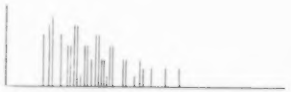
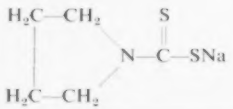
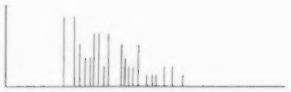
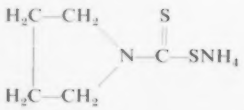
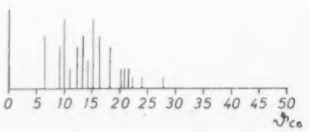
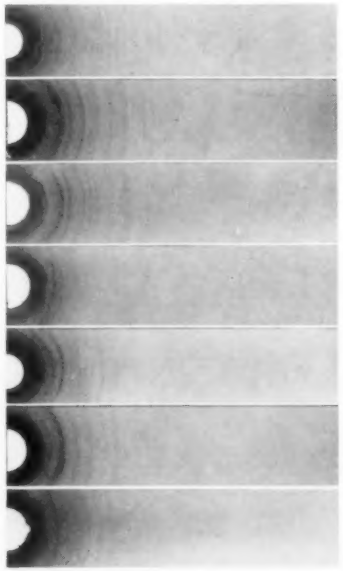
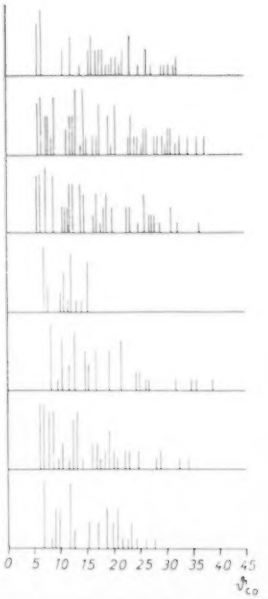
TAFEL IV. DISUBSTITUIERTE CARBAMATE

Carbamat	Kristallhabitus	Debye–Scherrer-Diagramme	
Natriumdiäthyl-dithiocarbamat 	doppelbrechende, rhomboedr. farblose Kristalle		
Ammoniumdiäthyl-dithiocarbamat 	doppelbrechende, prismat. farblose Kristalle		
Natriumpyrrolidin-dithiocarbamat 	doppelbrechende, prismat. farblose Kristalle		
Ammoniumpyrrolidin-dithiocarbamat 	doppelbrechende, prismat. farblose Kristalle		

TAFEL V. METALL-DIÄTHYLDITHIOCARBAMATE

Metall	Formel Verhältnis Me: Carbamat	Kristallhabitus der aus Chloroform umkristallisierten Verbindungen†	Debye–Scherrer-Diagramme
Ag	$Ag[(C_2H_5)_2NCS_2]$ 1:1	farblos, würfelförmig	
Cu	$Cu[(C_2H_5)_2NCS_2]_2$ 1:2	braun, langgestreckt, prismat.	
Zn	$Zn[(C_2H_5)_2NCS_2]_2$ 1:2	farblos, schw. gelb, prismat.	
Cr^{+3}	$Cr[(C_2H_5)_2NCS_2]_3$ 1:3	blau–violett, prismat.	
Mn	$Mn[(C_2H_5)_2NCS_2]_3$ 1:3	rotviolett prismat. pyramidenförmig	
Fe	$Fe[(C_2H_5)_2NCS_2]_3$ 1:3	braun–schwarz langgestr. prismat.	
U	$U[(C_2H_5)_2NCS_2]_6$* 1:6	rotgelb, würfelförmig	





† Symbol ⎯ ist gleich 10 μ für alle Metalle ausser für Zn, für das ist es 100 μ.
* Bruttoformel ist noch nicht sicher, der Kohlenstoffgehalt spricht aber für die angegebene Verbindung.

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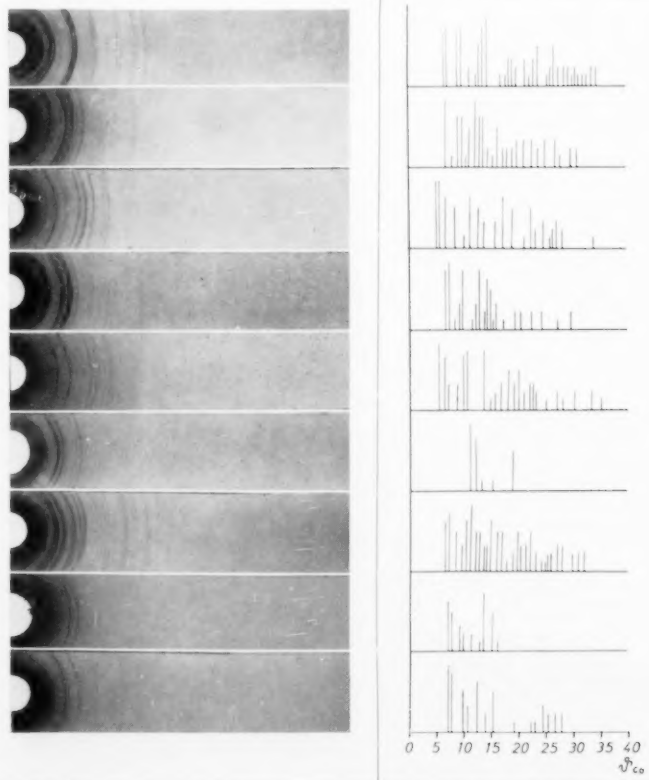
TAFEL VI. METALL-PYRROLIDINDITHIOCARBAMATE

Metall	Formel Verhältnis Me:Carbamat	Kristallhabitus der aus Chloroform umkristallisierten Verbindungen†	Debye–Scherrer-Diagramme
Cu	$Cu(C_5H_8NS_2)_2$ 1:2	braun–grün, kurz, prismat.	
Zn	$Zn(C_5H_8NS_2)_2$ 1:2	farblos, prismat.	
Cd	$Cd(C_5H_8NS_2)_2$ 1:2	gelb, büschelförmig, prismat.	
Ni	$Ni(C_5H_8NS_2)_2$ 1:2	grün, kurz, prismat.	
Bi	$Bi(C_5H_8NS_2)_3$ 1:3	blaugrün, unregelmässig, prismat.	
Mn	$Mn(C_5H_8NS_2)_3$	Schwach braun, unregelmässig	
Fe	$Fe(C_5H_8NS_2)_3$ 1:3	braun, sechs-seitig, pyramid. förmig	
Mo	$Mo(C_5H_8NS_2)_3$ 1:3	tief–violett, längl. prismat.	
Nb	$Nb(C_5H_8NS_2)_3$ 1:3	gelb, unregelmässig, prismat.	



† Symbol — ist gleich 10 μ.

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gefundenen überein. G. Peyronel[6] hat eine eingehende Studie über die Struktur des Ni-N-N-di-n-propyl-dithiocarbamates durchgeführt und für die Elementarzelle folgende Abmessungen gefunden: a = 25,20 Å, c = 8,30 Å c/a = 0,33 Å und das Volumen zu 4,564 Å^3. Auf eine Elementarzelle kommen 9 Moleküle. Die Elementarzelle gehört dem rhombischen System an.

Den *Tafeln IV, V und VI*, die neben den Bruttoformeln, dem Kristallhabitus auch die Debye-Scherrer-Diagramme zeigen, kann im Augenblick nichts hinzugefügt werden, genügen aber zur röntgenographischen Identifizierung, wenn unter gleichen Bedingungen gearbeitet wird. Genauere Strukturbestimmungen sind Gegenstand weiterer Untersuchungen, worüber später berichtet werden soll.

Summary—The empirical formulae, crystal habits and X-ray patterns for a number of metal-carbamate complexes are presented.

Résumé—Les auteurs décrivent l'aspect extérieur cristallin et donnent les formules empiriques et les diagrammes de rayons X d'un certain nombre de complexes métal-carbamate.

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A NEW SENSITIVE AND SPECIFIC TEST FOR VANADIUM^{V} WITH SULPHOSALICYLIC ACID

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Summary—A very sensitive and specific test for vanadium^{V} is described using sulphosalicylic acid as reagent. When this reagent is brought into contact with solid vanadium^{V} (a drop of the test solution evaporated to dryness on a watch glass) in the presence of concentrated sulphuric acid or 80% syrupy phosphoric acid, a blue colour is developed. Using this colour reaction, it is possible to detect 0·05 μg of vanadium^{V} in 0·05 ml of test solution. Aluminium^{III}, arsenic^{V}, beryllium^{II}, cadmium^{II}, chromium^{III}, chromium^{VI}, copper^{II}, iron^{III}, molybdenum^{VI}, nickel^{II}, tungsten^{VI}, uranium^{VI} and vanadium^{IV} do not interfere with this colour test, although some of them are known to form coloured complexes with sulphosalicylic acid under different conditions. Reducing agents like iron^{II}, uranium^{IV}, molybdenum^{V} and hydroquinone discharge the colour. The colour of the vanadium^{V}–sulphosalicylic acid compound is also discharged if the temperature is raised to 60°, though it reappears on cooling.

PANDU Ranga Rao and Gopala Rao[1] recently reported that quinquevalent vanadium develops at once a turquoise-blue colour when treated with salicylic acid in 20*N* sulphuric acid or syrupy phosphoric acid. This colour reaction, which was found to be almost specific, was utilised for the detection of very small amounts of vanadium^{V}. Cozzi and Raspi[2] found a somewhat similar colour reaction took place on treating vanadium with methyl salicylate in a medium containing hydrochloric acid, glacial acetic acid and acetic anhydride.

In this paper, a sensitive and a highly specific colour reaction is described for vanadium^{V} with sulphosalicylic acid in concentrated sulphuric acid or syrupy phosphoric acid. The colour developed by sulphosalicylic acid is both more sensitive and more stable than that with salicylic acid.

EXPERIMENTAL

Reagents

Sulphosalicylic acid, concentrated sulphuric acid or 80% syrupy phosphoric acid.

Procedure for the colour reaction in a test tube

One drop (0·05 ml) of vanadium^{V} solution and 1 drop of a 2% aqueous solution of sulphosalicylic acid are taken in a test tube, then concentrated sulphuric acid is added to make the total volume up to 2 ml. On mixing the contents, a greenish-blue colour develops immediately. The limit of identification was found to be 5 μg of vanadium^{V} in a total volume of 2 ml.

Effect of temperature and light on the stability of the colour

At room temperature (28°) the colour slowly faded with time, taking several days for complete discharge. On raising the temperature, the colour began to fade at about 60° and became pale green at 80°. The intensity was regained to some extent on cooling to room temperature. When heated to higher temperatures, the colour was completely lost and was not restored on cooling. These observations indicate that the colour development is caused by the formation of a complex (between vanadium^{V} and sulphosalicylic acid) which dissociates at higher temperatures and reforms on cooling. On heating to above 80°, vanadium^{V} probably oxidises sulphosalicylic acid quite rapidly.

There was no significant change in the intensity of the colour at room temperature even after exposure to bright sunlight for 15 min.

Effect of acid concentration

The colour did not develop at all if the sulphuric acid concentration was below 4·5*M*. Above this acidity, the intensity of the colour increases with increase in acid concentration.

When the reaction was carried out using phosphoric acid instead of sulphuric acid, a clear blue colour was obtained, this colour being more stable than the greenish-blue colour developed with sulphuric acid. Further, it was observed that the colour began to develop even from 4*M* acidity in a phosphoric acid medium, the intensity of the colour increasing with increase in acid concentration. In a hydrochloric, nitric, perchloric or glacial acetic acid medium, the colour did not develop when aqueous solutions of vanadium^{V} and sulphosalicylic acid were used. However, it was possible to obtain a positive test for vanadium in these media if ammonium vanadate and sulphosalicylic acid were mixed in the solid state.

It is interesting to note that a bluish-black product is formed immediately on mixing solid ammonium vanadate with solid sulphosalicylic acid (but not with salicylic acid, acetylsalicylic acid, phenyl salicylate or methyl salicylate).

Interferences

Aluminium^{III}, arsenic^{V}, beryllium^{II}, cadmium^{II}, chromium^{III}, chromium^{VI}, copper^{II}, iron^{III}, molybdenum^{VI}, nickel^{II}, tungsten^{VI}, uranium^{VI} and vanadium^{IV} do not interfere with the test, although some of these ions are known to form coloured complexes with sulphosalicylic acid under different conditions. Cerium^{IV} and manganese^{VII} do not interfere with this colour reaction for vanadium^{V} provided a sufficient excess of the reagent is present. Substances like iron^{II}, uranium^{IV}, molybdenum^{V}, hydroquinone, *etc*, which reduce vanadium^{V}, should be absent.

Spot test procedure

If aqueous solutions of vanadium^{V} and sulphosalicylic acid are used for the test on a spot plate, the test is not very sensitive because of the two factors mentioned already, namely, the increase of temperature and lowering of acidity, both resulting from the dilution of the acid. However, the sensitivity can be very greatly increased by carrying out the test as follows:

One drop (0·05 ml) of the test solution is taken on a watch glass and evaporated to dryness on a water bath. After the watch glass has cooled to room temperature, 2 drops of concentrated sulphuric acid (or 80% syrupy phosphoric acid) are placed on the watch glass at a little distance from the residue and a small crystal of sulphosalicylic acid is intimately mixed in this acid. The mixture is allowed to flow on to the residue of vanadium^{V} by keeping the watch glass slightly inclined. At the boundary where the reagent mixture meets the residue of vanadium^{V} test solution, a fine blue line appears.

Limit of identification: 0·05 μg of vanadium^{V} per 0·05 ml of test solution.

Dilution limit: 1:1,000,000.

Acknowledgment—The authors wish to thank Prof. G. Gopala Rao for his interest in this work.

Zusammenfassung—Ein sehr empfindlicher Nachweis für Vandin(V) wird beschrieben. Wenn Sulfosylicylsäure mit festem Vanadin(V) salz (ein Tropfen Probelösung auf einem Uhrglas zur Trockene eingedampft) in Kontakt gebracht wird, entwickelt sich in Gegenwart von conc. Schwefeloder 80%iger Phosphorsäure eine blaue Färbung. Mittels der Reaktion ist es möglich 0·05 μg Vanadin(V) in 0·05 ml Lösung nachzuweisen. Al, As(V), Be, Cd, Cr(III), Cr(VI), Cu, Fe(III), Mo(VI), Ni, W(VI), U(VI) und V(IV) stören nicht, obwohl bekannt ist, dass manche der Ionen gefärbte Komplexe mit dem Reagens geben, wenngleich unter anderen Bedingungen. Reduzierende Reagenzien, wie Fe(II), U(IV), Mo(V) oder Hydrochinon bleichen die Farbe aus. Die Färbung verschwindet bei Erhitzen auf 60°C, erscheint jedoch beim Abkühlen wieder.

Résumé—Les auteurs décrivent une recherche du vanadium (V) très sensible et spécifique, utilisant l'acide sulfosalicylique comme réactif. Quand ce réactif est mis en contact avec du vanadium (V) solide (une goutte de la solution à essayer évaporée jusqu'à siccité sur un verre de montre), en présence

d'acide sulfurique concentré ou d'acide phosphorique sirupeux à 80%, il apparaît une couleur bleue. En utilisant cette réaction colorée, il a été possible de déceler 0,05 μg de vanadium (V) dans 0,05 ml. L'aluminium(III), l'arsenic(V), le béryllium(II) le cadmium(II), le chrome(III), le chrome(VI), le cuivre(II), le fer (III), le molybdène(VI), le nickel(II), le tungstène(VI), l'uranium(VI), le vanadium(IV) ne gênent pas cette réaction colorée, bien que certains d'entre eux soient connus pour former des complexes colorés avec l'acide sulfosalicylique dans différentes conditions. Les agents réducteurs comme le fer(II), l'uranium(IV), le molybdène(V), l'hydroquinone déchargent la couleur. La couleur du composé vanadium(V)-acide sulfosalicylique est aussi déchargée, si la température est élevée jusqu'à 60°, quoiqu'elle réapparaisse au refroidissement.

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TRIFLUOROMETHYL SULPHONIC ACID AS A TITRANT IN GLACIAL ACETIC ACID SYSTEMS

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Summary—Trifluoromethyl sulphonic acid in glacial acetic acid has been compared with perchloric acid in glacial acetic acid as a titrant in a limited number of cases. It does not appear that the reagent is likely to compete seriously with perchloric acid in non-aqueous titrimetry. Although comparable to perchloric acid in acid strength in acetic acid as well as in instrument response, it is unlikely that the considerably higher cost can be justified on the grounds of freedom from precipitate formation alone and no other advantageous feature has been observed which could justify this.

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SEVERAL aliphatic and aromatic sulphonic acids have recently been examined[1] as titrants for use in glacial acetic acid systems. None of these have proved to be as useful as perchloric acid as a titrant in this medium but it is quite practicable to use them as they possess, as a class, the advantage of ensuring freedom from precipitate or gel formation when certain compounds are titrated. Potassium hydrogen phthalate, for example, the common primary standard for use in glacial acetic acid systems, persistently forms a precipitate with perchloric acid during titration, and this can lead to difficulties in some instrumental methods of end-point detection.

Trifluoromethyl sulphonic acid has recently been prepared[2] and described as one of the strongest known sulphonic acids; and it may even be one of the strongest of all known acids. In view of the interest shown in comparatively weak sulphonic acids as titrants, a comparison of the analytical possibilities of trifluoromethyl sulphonic acid with the conventional perchloric acid in glacial acetic acid has been made, using a representative selection of basic substances and experimental techniques.

EXPERIMENTAL

Reagents and apparatus

Perchloric acid, 0·1N in glacial acetic acid: B.D.H. commercially available material was used, freshly standardised against potassium hydrogen phthalate.

Trifluoromethyl sulphonic acid, 0·1N in glacial acetic acid: Potassium trifluoromethyl sulphonate* (4·5 g) and concentrated sulphuric acid (6 ml) were heated together in a microdistillation apparatus under reduced pressure (2 mm Hg). Distillation was stopped when the oil bath temperature reached 120°. The distillate consisted of 2 ml of a clear, fuming liquid and a white solid (presumably trifluoromethyl sulphonic acid monohydrate,[3] which can be distilled from sulphuric acid) adhering to the receiver. The trifluoromethyl sulphonic acid was decanted from the solid, weighed, and diluted with glacial acetic acid to the requisite volume. It was standardised against potassium hydrogen phthalate.

Indicators: 0·5% solutions in glacial acetic acid of Crystal Violet, Oracet Blue B and α-naphtholbenzein were used. The end-point shade obtained with the different compounds titrated was matched against that obtained during standardisation with the same indicator.

Potentiometric titrations. A sleeve-type calomel electrode and a glass electrode were used in conjunction with a direct-reading pH meter (Electronic Industries Ltd. Model 23). End-points were determined graphically.

* Kindly supplied by The Minnesota Mining and Manufacturing Co. Ltd.

High-frequency titrations: The simple one-valve instrument[4] operating at 15 Mc/s modified as previously described[5] was used. Owing to the precipitation of potassium perchlorate during titrations with perchloric acid, diphenylguanidine was preferred as the primary standard for use with this method of end-point detection rather than potassium hydrogen phthalate, which was used for the visual and potentiometric standardisations.

RESULTS

A comparison of the potentiometric titration curves obtained with trifluoromethyl sulphonic acid and perchloric acid in glacial acetic acid with diphenylguanidine and potassium hydrogen phthalate as standards is given in Fig. 1. The shape of the high-

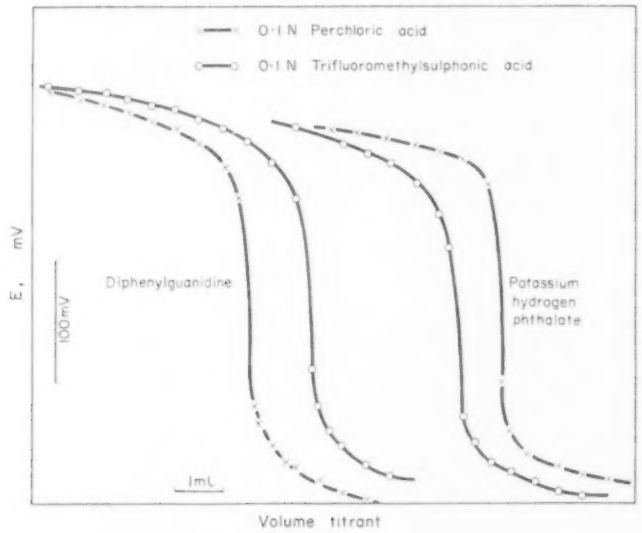

FIG. 1.

frequency titration curves obtained in the titration of diphenylguanidine and decamethylene-bis-pyridinium nitrate with both titrants is shown in Fig. 2. Results obtained with trifluoromethyl sulphonic acid for the determination of equivalent weights of a number of basic compounds of widely different constitution, on a semi-micro scale, are recorded in Table I.

Five separate determinations of the equivalent weight of a sample of commercial trinonylamine with both perchloric acid and trifluoromethyl sulphonic acid using Oracet Blue B as visual indicator gave the results shown in Table II.

DISCUSSION

The results show that perchloric and trifluoromethyl sulphonic acids are comparable titrants in glacial acetic acid systems. In potentiometric titrations trifluoromethyl sulphonic acid behaves as a very strong acid, and the height of the potential break and the maximum value of dE/dV (the rate of change of potential with volume of titrant) were almost identical with those obtained using perchloric acid. In this respect trifluoromethyl sulphonic acid is superior to the other sulphonic acids so far tested. As with other sulphonic acids, there was no trace of precipitation or gel formation when using potassium hydrogen phthalate as a primary standard, or indeed with any of the compounds so far examined.

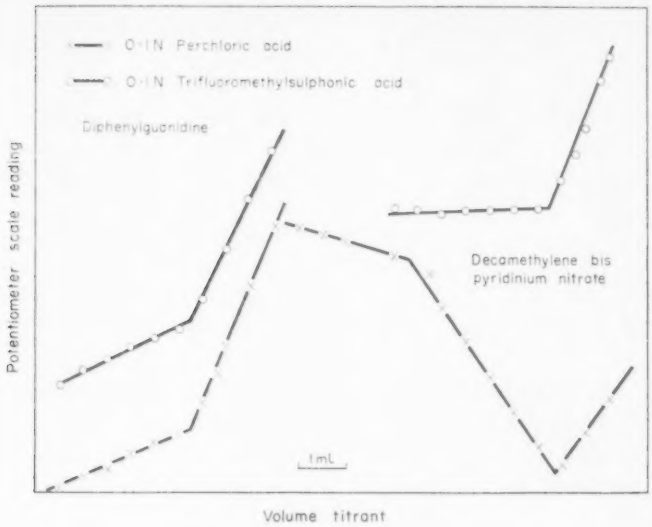

FIG. 2.

TABLE I

Compound	Method	Equivalent wt	
		Found	Required
Guanidine carbonate	Visual—α-naphthol-benzein	92	90
Ephedrine	Visual—α-naphthol-benzein	175	174
Diphenylguanidine	Visual—Oracet blue B	210	211
Diphenylguanidine	Potentiometric	211	211
Decamethylene-bis-pyridinium nitrate	High-frequency	210	211
Decamethylene-bis-pyridinium nitrate	Potentiometric	211	211
o-Phenanthroline hydrate	Visual—Oracet blue B	198	200
Tri-iso-octylamine	Visual—Oracet blue B	351	353

TABLE II

Titrant	Mean	Standard deviation	Required
Perchloric acid	399	3·6	395
Trifluoromethyl sulphonic acid	396	1·5	395

Using the high-frequency method of end-point indication, there was a slight advantage to be gained by the use of perchloric acid, as evidenced by the smaller angle between the intersecting lines obtained approaching and retiring from the end-point. Furthermore, whereas with perchloric acid information can often be gained from high-frequency titrations concerning the functionality of the compound being titrated, this effect was not noted when trifluoromethyl sulphonic acid was used. Decamethylene-bis-pyridinium nitrate, for example, gave two distinct end-points with

perchloric acid, corresponding to the titration of first one, and then both quaternary functions, but only one end-point, that corresponding to two quaternary groups, was detected during titration with trifluoromethyl sulphonic acid.

With visual indication of the end-points the precision obtained in the titration of trinonylamine with trifluoromethyl sulphonic acid was slightly better than when perchloric acid was used. The new titrant, however, was not as effective as perchloric acid for the titration of quaternary ammonium halides using the mercuric acetate method with Crystal Violet as indicator. When a representative selection of quaternary ammonium and phosphonium halides were titrated with trifluoromethyl sulphonic acid, only diffuse end-points were obtained. Several basic compounds were titrated visually with the new titrant, and satisfactory values of their equivalent weights were obtained.

Although new uses of trifluoromethyl sulphonic acid are being developed, it would appear doubtful from this limited assessment whether it will ever seriously compete with perchloric acid for use in non-aqueous titrimetry. Although comparable to perchloric acid in acid strength in acetic acid, as well as in instrument response, it is unlikely that the considerably higher cost can be justified on the grounds of freedom from precipitate formation alone, and no other advantageous feature has been observed which could justify this.

Zusammenfassung—Trifluoromethylsulfonsäure in Eisessig wurde mit Perchlorsäure in Eisessig als Titrationsmittel verglichen. Es scheint nicht wahrscheinlich, dass das Reagens ernsthaft mit Perchlorsäure als Titrationmittel in nichtwässrigem Medium konkurrieren kann. Das Reagens ist zwar mit Perchlorsäure vergleichbar, soweit es die Stärke (in Essigsäure) und das Ansprechen des Instrumentes betrifft; es ist aber unwahrscheinlich, dass sich die beträchtlich höheren Kosten lediglich wegen Nichtauftretens von Niederschlägen rechtfertigen lassen. Dies ist der einzige auffindbare Vorteil.

Résumé—L'auter a comparé l'acide trifluorométhylsulfonique dans l'acide acétique glacial à l'acide perchlorique dans le même solvant comme agent titrant dans un nombre limité de cas. Il ne semble pas probable que ce réactif concurrence sérieusement l'acide perchlorique dans la titrimétrie en milieu non aqueux. Bien que comparable à l'acide perchlorique au point de vue de sa force dans l'acide acétique, il est improbable que son coût très élevé puisse être justifié par la seule raison qu'il ne se forme pas de précipité et qu'aucun autre avantage n'ait été observé qui pourrait légitimer son utilisation.

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A STUDY OF THE CERIUM^{III}-ALIZARIN COMPLEXAN–FLUORIDE REACTION

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Summary—The optimum pH range of the cerium^{III}-alizarin complexanate method for fluoride has been established as pH 5·0–5·2 at which value the method may be applied over a wide concentration range from 5 μg of fluoride ion (0·1 ppm) to 1·6 mg (>160 ppm) using a conventional spectrophotometer. The nature of the changes produced in the colour system by variation of pH are briefly discussed and the interference of 23 selected cations and 3 common anions has been examined. Practically all of the serious cationic interference can be overcome by the simple addition of a masking agent but, in a few cases, a preliminary extraction with 8-hydroxyquinoline and chloroform is required.

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ALIZARIN complexan, 3[di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone, was first prepared for use as a complexometric indicator[1,2] but it was later observed that the red chelates formed with cerium^{III}, lanthanum and praseodymium (and to a lesser extent with samarium) yielded blue water-soluble complexes with fluoride ion.[3] The cerium^{III} chelate was selected for further qualitative and quantitative studies.[4,5,6] The structure of the ternary complex has recently been defined and reasons for the unusual selectivity have been proposed.[7]

In the present investigation, the range has been extended from microgram to milligram amounts, and the effect of pH and time for the development of a stable colour have been studied more closely. The influence on the reaction of other ions which were not previously examined, or only examined superficially, has been established. Certain ions interfere seriously, but, in most instances, this effect can be overcome by the application of simple masking reactions.

Optimum pH range

In earlier work[4,5,7] the reaction between fluoride and cerium^{III}-alizarin complexanate was carried out at pH 4·3, because at this pH the yellow to red acid-base transition of alizarin complexan just becomes apparent. Because the reaction was adjudged to be sufficiently sensitive (*ca* 0·1 ppm) and visually most easily observed at this pH, no further examination was then made of the permissible pH range. A study of this aspect is important, however, as will be seen subsequently.

In these experiments, sensitivity tests were carried out on fluoride ion at various pH levels using $5 \times 10^{-4}M$ solutions of alizarin complexan and cerium^{III} prepared by reduction of cerium^{IV} ammonium nitrate. A very slight excess of alizarin complexan was maintained over the normal 1:1 mole ratio with respect to cerium^{III}. These experiments extending from pH 3·5–12 indicated clearly (Fig. 1) that the optimum sensitivity of the fluoride reaction measured against the cerium^{III} chelate occurs at pH 5·0–5·2. In these particular experiments the solutions were only very lightly buffered with an acetic acid/acetate mixture (pH 4·3) and the pH was adjusted to the necessary value, using a pH meter, by careful addition of 1M sodium hydroxide or

1*M* hydrochloric acid. The effect of acetate ion recorded by other workers[6] was observed, *viz.* stronger absorption at lower acetate ion concentration, but when later experiments were repeated using normal buffer formulations and normal 1:1 cerium to reagent ratio, optimum sensitivity was again found to lie in the pH range 5·0–5·2. Fig. 2 shows a cross section of the alteration in shape of the absorption curves produced by variation of pH in these initial experiments. Increase of hydroxyl ion concentration produces a hyperchromic effect on both the cerium^{III}-alizarin complexanate and the ternary fluoride complex. At pH 3·5 [Fig. 2(a)] both the cerium^{III} chelate and the

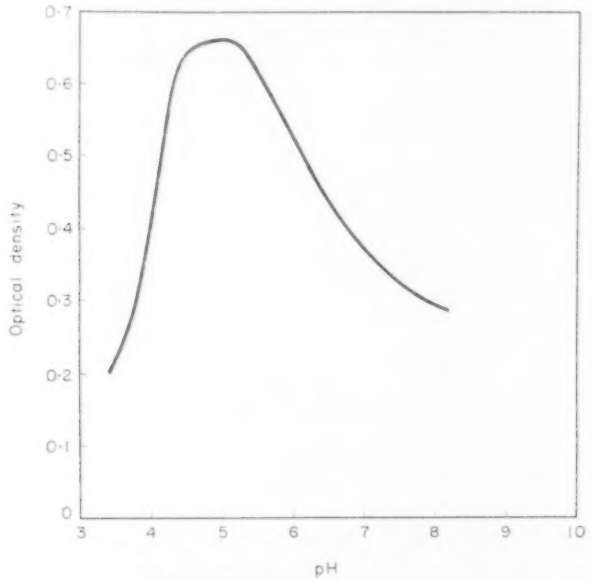

FIG. 1.—Influence of pH on sensitivity.
50 μg of F^- measured by procedure (A) in 4-cm cuvette against cerium^{III}-alizarin complexanate at 610 mμ.

fluoride complex are largely dissociated as can be seen from the presence of the strong absorption band for free alizarin complexan at *ca.* 430 mμ, but at pH $\geqslant$ 4·0 [Fig. 2(B), (C), (D)] this band disappears. Fig. 3 shows the marked tendency for occurrence of a bathochromic shift of the wavelength of maximum band absorption for both the cerium^{III} chelate and the fluoride complex with increase of pH, over the range 3·5–6·2. Thereafter, the cerium^{III} chelate maintains a more or less unchanged wavelength of maximum absorption showing only a hyperchromic effect probably because of increased dissociation of the proton on the 1-hydroxyl group (*cf* Fig. 4).

On the other hand, from pH 6–12 there is observed for the fluoride complex a hyperchromic shift as above, and also a distinct hypsochromic change of wavelength of maximum absorption. This suggests that hydrolysis of the ternary fluoride complex (Fig. 4(d)) is occurring with replacement of the fluoride ion by hydroxyl.

In summary, these data indicate clearly that the method should not be operated beyond the range pH 4–6 and that the optimum sensitivity occurs at pH 5·0–5·2. At this dilution using $5 \times 10^{-4}M$ solutions of cerium^{III} and reagent, the time taken for stable colour development by the recommended procedure [*procedure*(*A*)] is 15 min

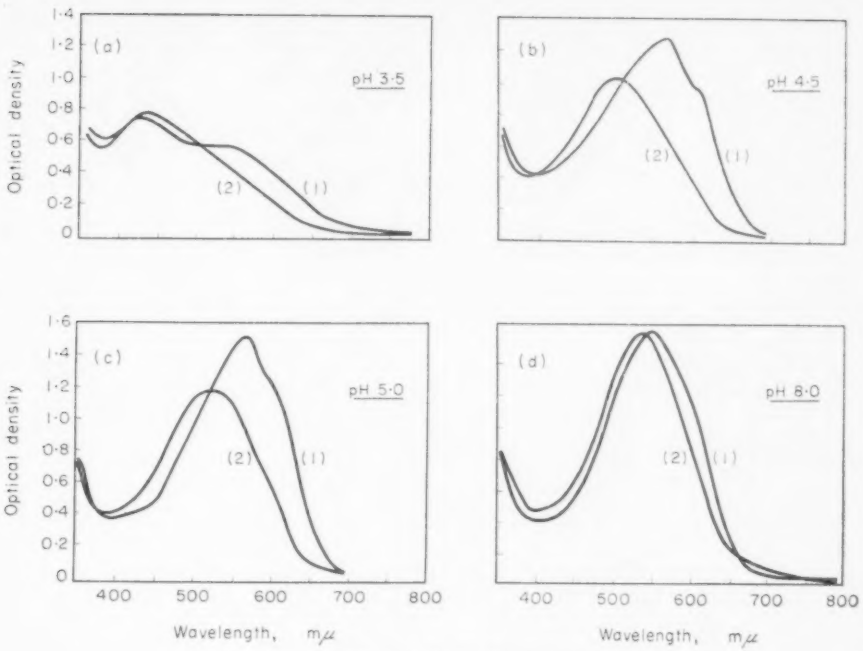

FIG. 2.—Effect of pH on absorption curves
(1) Ternary fluoride complex.
(2) Cerium^{III}-alizarin complexanate.
(A) pH 3·5; (B) pH 4·5; (C) pH 5·0; (D) pH 8·0.

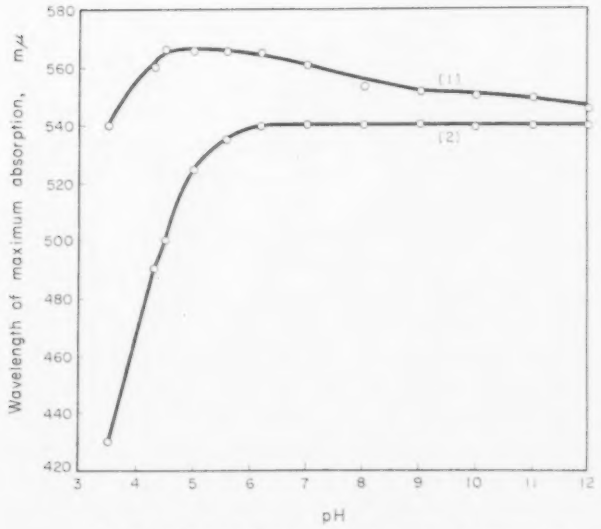

FIG. 3.—Influence of pH on maximum band absorption
(1) Ternary fluoride complex.
(2) Cerium^{III}-alizarin complexanate.

for the fluoride complex and 60 min for the cerium^{III} chelate against which it is measured. Once prepared, both colour systems remain unchanged for several days. Consequently it is recommended that a safe development time of 60–90 min should be allowed.

Concentration range

In earlier papers[5,7] on the spectrophotometric determination of fluoride at pH 4·3, Beer's law was obeyed over the range 5–40 μg when the calibration curve was prepared from the recommended amounts of $5 \times 10^{-4}M$ solutions of cerium^{III} nitrate and

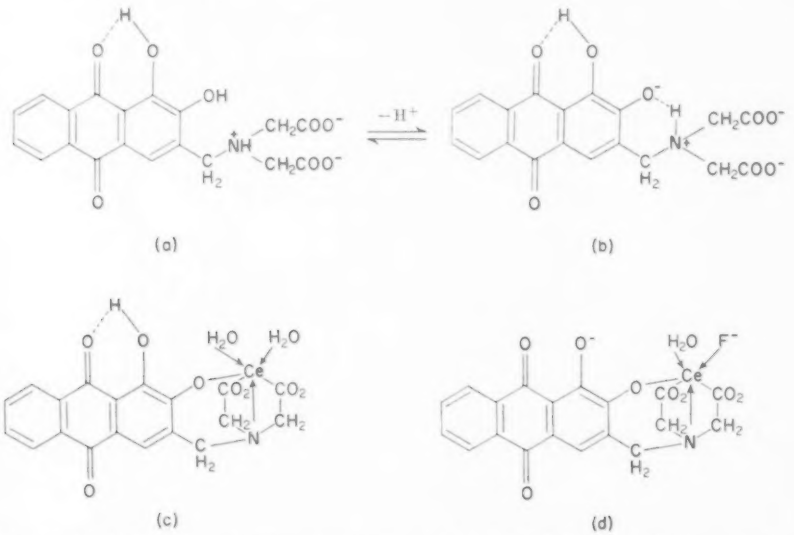

FIG. 4.—At pH 5·0–5·2 alizarin complexan exists as a mixture of the two ionisation stages (a) and (b); (c) cerium^{III}-alizarin complexanate; (d) ternary fluoride complex.

alizarin complexan. Subsequently, in applying the method to the semimicro scale, Johnson and Leonard[6] did not attempt to use stronger reagent formulations but took an aliquot of the fluoride solution resulting from the decomposition of the compound, to obtain amounts of fluorine falling within the range of the submicro calibration curve, *i.e. ca.* 25 μg. This may involve dilution factors of more than 200 in some cases. Bartkiewicz and Robinson[8] used the method over the range up to 10 ppm, but commented that at higher concentrations of fluoride ion the colour was bleached out. This observation indicates that insufficient attention was paid to the nature of the ternary fluoride complex and in all probability insufficient cerium^{III}-alizarin complexanate was added. The fact that large amounts of fluoride added to a fixed amount of the cerium^{III} chelate bleach the blue colour of the fluoride complex back to the free yellow alizarin complexan has already been stated by Leonard and West[3,7] and is an obvious result of mass action and the insolubility of cerium^{III} fluoride. Because no serious attempt has been made to determine larger than microgram amounts of fluorine by this method, a series of experiments was initiated in which the concentration of all of the reagents involved was systematically increased in a step-wise fashion by factors of 10.

With $5 \times 10^{-3}M$ solutions of cerium^{III} nitrate and alizarin complexan, and a standard fluoride solution containing 50 μg/ml, calibration curves were obtained up to 500 μg. The calibration curve obeyed the Lambert–Beer law from 50–275 μg; the straight line extension did not pass through the origin, but made a negative intercept on the optical density axis. This reaction [*Procedure* (*B*)] was carried out at pH 5·0–5·2 and measurements were made in 2-mm cuvettes at 620 mμ which was the wavelength of maximum absorption of the fluoride complex measured against reagent.

When larger amounts of cerium^{III} and reagent were used, but still maintaining their 1:1 mole ratio [*Procedure* (*C*)], a linear calibration curve was obtained over the range 100–550 μg; up to 1000 μg the points still fall on a smooth curve falling only slightly below the linear projection of the lower part of the curve.

Finally, experiments were carried out with $10^{-2}M$ solutions of cerium^{III} and reagent at pH 5·2. The wavelength of maximum absorption for the fluoride complex measured against the cerium^{III} chelate now shifted to 630 mμ and once prepared, remained unchanged for more than 4 days. The calibration curve followed the same pattern, being linear up to 800 μg and still lying on a smooth curve up to 1600 μg. No attempt was made to extend the upper range of the method beyond this point.

It is appropriate here to mention that the pH and permissible concentration ranges are inter-related. Thus, whilst the method operates satisfactorily at pH 4·3 with $5 \times 10^{-4}M$ solutions, precipitation occurs at this pH with $5 \times 10^{-3}M$ solutions, particularly with the cerium^{III} chelate alone and with the lower amounts of fluoride ion. At pH 5·0–5·2 this difficulty is not encountered even with $10^{-2}M$ solutions. This effect of pH and the higher solubility of the fluoride complex compared to the cerium^{III} chelate agrees well with the proposed structure and protolysis mechanism suggested previously by Leonard and West.[7] The minimum reaction time employed throughout these studies was 60–90 min though qualitatively the reaction appeared to proceed more rapidly in the more concentrated solutions.

Interferences

In the paper describing the spot-test procedure for fluoride[4] it was found that the colour produced by 0·2 μg of fluoride was not interfered with visually by one hundred-fold mole ratios of sulphate, sulphide, chloride, bromide, iodide or cyanide. A six-fold excess of phosphate and the presence of moderately powerful complexing agents,such as iminodiacetic acid, partly suppressed the colour reaction whilst oxalate, citrate tartrate, uramildiacetic acid and EDTA interfered completely at 1:1 ratios. In addition, it was found that aluminium, cobalt^{II}, copper^{II}, nickel, lead, iron^{III} and zinc prevented the formation of the blue colour. A ten molar amount of calcium caused slight inhibition whereas one hundred-fold excesses of mercury^{II}, manganese and magnesium showed no visible effect.

In quantitative experiments, a later study[6] tested the interference of a few ions in the determination of 26 μg of fluoride ion at pH 4·6. A 10% interference occurred with the following ions at the stated mole ratios: aluminium, 0·19; iron^{III}, 0·105; citrate, 0·36; phosphate, 7·7.

In the experiments described below interferences were tested mainly at the 1:1 mole ratio on a test solution containing 500 μg of fluoride ion. The results shown in Table I were obtained by the addition of the interfering ion to the fluoride solution and allowing the two to react for 30 min. Then in each case were added, successively, 25 ml

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of $6{\cdot}25 \times 10^{-3}M$ alizarin complexan solution, 5 ml of buffer solution (pH 5·2) and 25 ml of $5 \times 10^{-3}M$ cerium^{III} nitrate solution; the solution was allowed to stand overnight following dilution to 100 ml. At this point it should be noted that the interference can operate in any one (or combination) of three main ways: (1) formation of a stable complex with fluoride ion, thus preventing the formation of the blue colour; (2) formation of a more stable chelate than cerium^{III} with alizarin complexan, thus decreasing or increasing the absorption at 620 mμ according to its molecular extinction coefficient and wavelength of maximum absorption; (3) by formation of a stable complex with cerium^{III}, almost invariably decreasing the absorption at 610 mμ. For example a small amount of aluminium may cause a decrease by virtue of process (1) whilst a large amount may give high values by (2). The possibility also exists for a compensation of errors to result in no apparent interference though such a process would be unusual. Since most metal ions react to form complexes containing more than one fluoride ion and an excess of the interfering ion relative to fluoride requirements would therefore be present in all cases, an excess of *free* alizarin complexan was formulated in these particular experiments. This minimises the possibility of compensation by enhancing the absorbance of the foreign metal chelate without diminishing that of the cerium^{III} chelate unduly.

TABLE I. INTERFERENCE OF VARIOUS IONS WITH FLUORIDE METHOD. THE RATIO $[M^{n+}]/[F^-] = 1$, EXCEPT WHERE STATED OTHERWISE. (500 μg F^-)

Ion	Amount taken, μg [Atomic ratio]	Interference, %	Ion	Amount taken, μg [Atomic ratio]	Interference, %
Ag	2806	2·5	Mg	632	1·4
Al	701	8	Mn^{II}	1429	13·7
As^{V}	1948	0·5	Ni	1526	145
Be	234	−54	Pb	5388	67·9
Ba	3573	2·5	Sr	2278	1·5
Ca	1045	−10·2	Tl^{I}	5314	1·0
Cd	2922	92·5	V^{V}	1324	10·0
Co	1532	135	Zn	1700	83·5
Cr^{III}	2700 [2]	51·4	Zr	2372	1·6
Cu^{II}	1653	64			
Fe^{II}	1452	116	B (as borate)	1125 [4]	−10
Fe^{III}	1452	109	PO_4^{3-}	2471	−8
Hg^{I}	5216	18·9	SO_4^{2-}	24,970 [10]	0·5
Hg^{II}	5216	7·0			

Large positive interferences occur with cadmium, cobalt^{II}, chromium^{III}, copper^{II}, iron^{II}, iron^{III}, nickel, lead, zinc and moderate interferences from aluminium, mercury^{I}, mercury^{II}, manganese^{II} and vanadium^{IV}. Large negative interferences occur with beryllium and moderate interferences from calcium, borate and phosphate. The interference of silver, arsenic^{V}, barium, magnesium, strontium, thallium^{I}, zirconium and sulphate does not appear to be serious. The moderate nature of the interference of aluminium and zirconium is surprising in view of the well known stability of their fluoride complexes; partial compensation may well account for the observed results because both also form stable chelates with alizarin complexan.

Elimination of interferences

In studying the elimination of interferences the normal 1:1 ratio of cerium^{III} to alizarin complexan was maintained and the normal procedure for 500 μg of fluoride [*Procedure* (*C*)] was followed with the amounts of interference specified in Table I.

An attempt was made first of all to add just sufficient EDTA to the test solution containing fluoride to complex the interfering metal ions. The necessary amount was found by complexometric titration on a separate aliquot of solution. In no experiment was this measure successful; low results were invariably found because of the partial complexing of the cerium^{III} by EDTA, in spite of the presence of the other free metals which had previously reacted with it.

Potassium cyanide masking was successful as specified for the complete elimination of the interference from copper^{II}, cobalt^{II}, mercury^{I} and mercury^{II}, and was only slightly unsatisfactory for manganese^{II}. The interference from cadmium and zinc was not entirely removed.

2,3-Dimercaptopropanol (BAL) completely eliminated the interference of nickel and lead. Similarly, an excess of sodium sulphide removed the interference of cadmium, zinc, and lead.

Aluminium was not masked by sodium diethyldithiocarbamate, tartrate or triethanolamine; iron^{III} was not masked by tartrate or by *o*-phenanthroline in the absence or presence of ascorbic acid; beryllium was not masked by phosphate or (added) acetylacetone; chromium^{III} was not masked by tartrate, calcium by *o*-phenanthroline or vanadium^{V} by reduction with ascorbic acid.

Because most of the metals which still interfere are known to react well with general-purpose reagents, such as cupferron and 8-hydroxyquinoline, attempts were made to add these as masking agents, but both caused interference with the control, particularly cupferron. Further experiments using 8-hydroxyquinoline revealed that this interference was caused by attack from the *excess* of reagent on the cerium^{III} and another series of tests was effected in which the excess of 8-hydroxyquinoline and the interfering metal-chelate were extracted at pH 5·0–5·2 *before* the addition of alizarin complexan and cerium^{III} nitrate. The interferences of aluminium, iron^{III}, chromium^{III}, and vanadium^{V} were completely removed by this simple expedient. Zirconium proved troublesome because of extremely stable emulsion formation, but it is known to be extracted[9] under the conditions and consequently no further attempt was made to eliminate the emulsion formation since this is probably only a point of detail.

Calcium and beryllium are the only two remaining cationic interferences amongst the metals tested. They were not accounted for in this study, but it is logical to assume that their interference could readily be eliminated by a closely similar process. Calcium may be extracted as its 8-hydroxyquinolate by chloroform at higher pH values[9] and beryllium by the closely related agent 8-hydroxyquinaldine also in chloroform at pH 7·5–8·5.[10] It is not known how well the beryllium would extract from a fluoride-containing solution, but in view of the performance of aluminium and iron^{III}, the procedure would be expected to be entirely successful for calcium if not also for beryllium. Another possibility which exists for beryllium is the extraction of its acetylacetone chelate at low pH.[11] Removal of the excess acetylacetone by extraction would doubtless remove the interference noted during the direct addition experiments described earlier in this paper (*cf.* also the direct addition of 8-hydroxyquinoline).

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The extraction method based on 8-hydroxyquinoline should eliminate the cationic interference of a much wider range of metals than those examined in this study. Lastly, the removal of anionic interference by borate or phosphate would most probably require an ion-exchange separation, though the masking of borate interference by mannitol may be possible.

CONCLUSION

It has been shown that the optimum sensitivity of the cerium^{III}-alizarin complexan method for fluoride is obtained at pH 5·0–5·2. The working range of the method by suitable modification lies between 5 μg (0·1 ppm) to more than 1·6 mg (>160 ppm) at this pH range. Whilst the method works satisfactorily at pH 4·3 for dilute solution work, precipitation of the cerium^{III} chelate occurs at that pH when using $\geq 5 \times 10^{-3}M$ reagents. The wavelength of maximum absorption for measurement of the ternary fluoride complex against the cerium^{III} chelate shifts from 610 mμ with $5 \times 10^{-4}M$ to 620 mμ for $5 \times 10^{-3}M$ to 630 mμ for $10^{-2}M$ solutions.

The interference of 23 selected cations has been studied. In most instances it has been shown that the addition of a suitable masking agent, such as cyanide, 2,3-dimercaptopropanol or sulphide prevents interference, whilst for ions which are more difficult to mask, such as aluminium, chromium^{III} and vanadium^{V}, a simple preliminary extraction with 8-hydroxyquinoline and chloroform removes all interference.

EXPERIMENTAL

Reagents

$5 \times 10^{-4}M$ *Alizarin complexan solution*: Suspend 192·5 mg of alizarin complexan (a suitable grade of reagent is obtainable from Hopkin and Williams Ltd.), in freshly distilled water and add the minimum amount of 2*N* sodium hydroxide solution to ensure complete solution of the solid. Add dilute hydrochloric acid carefully till the violet colour of the solution turns to red (pH 5–6) and dilute to 1 litre.

Stronger solutions, *e.g.* $5 \times 10^{-3}M$, are prepared with proportionate amounts of reagent. Magnetic stirring is advisable to ensure complete solution and the colour in the flask should remain (just) violet to ensure complete solution before cautious addition of the hydrochloric acid during which the solution should be well mixed or agitated.

$5 \times 10^{-4}M$ *Cerium^{III} nitrate solution*: Prepare a solution of AnalaR cerium^{IV} ammonium nitrate (*ca.* 55 g/litre) and titrate against standard iron^{II} ammonium sulphate using ferroïn as indicator. Dilute this stock solution to be exactly 0·1*M*. Take a suitable aliquot of the stock dilution, reduce to cerium^{III} by the addition of an excess of freshly prepared ascorbic acid solution and dilute to the mark. $5 \times 10^{-3}M$ cerium^{III} nitrate solution is similarly prepared.

Buffer solution (pH 5·0–5·2): Dissolve 100 g of AnalaR sodium acetate trihydrate in distilled water and add 11 ml of glacial acetic acid (pH meter 5·2). Dilute to 1 litre.

Standard fluoride solution: Dissolve 221·1 mg of (BDH extra pure) sodium fluoride in distilled water and dilute to 1 litre. This solution contains 100 μg of F^- per ml. More dilute solutions, *e.g.* 5 and 50* μg/ml, may be prepared by dilution.

$2{\cdot}6 \times 10^{-2}M$ *Solutions of interfering ions*: Iron^{III} ammonium sulphate, nickel sulphate, copper chloride, calcium chloride, *etc.*

$2 \times 10^{-1}M$ *Potassium cyanide solution*: 1·3 g of potassium cyanide in 100 ml of water.

$5 \times 10^{-2}M$ *Sodium sulphide solution*: 1·2 g of $Na_2S.9H_2O$/100 ml of water.

10% 2,3-*Dimercaptopropanol solution*: 10% V/V in aqueous ethanol.

2·26% 8-*Hydroxyquinoline solution*: 2·26 g in 100 ml of ethanol.

Chloroform

* $2{\cdot}632 \times 10^{-3}M$ sodium fluoride solution contains 50 μg/ml of F^-.

Apparatus

Unicam SP 600 spectrophotometer: With 4-cm and 2-mm cuvettes. The instrument was operated from the mains electricity supply via a stabilised 12V transformer.

Procedures

Procedure (A): 5–50 μg *of fluoride ion* (610 mμ).

Pipette 1–10-ml aliquots of a 5 μg/ml fluoride solution into 100-ml standard flasks, add 10 ml of $5 \times 10^{-4}M$ alizarin complexan solution and 2 ml of buffer solution (pH 5·0–5·2) from pipettes to each flask, followed by 10 ml of $5 \times 10^{-4}M$ cerium^{III} solution with constant swirling of the contents of the flask during the addition of the latter. Dilute the contents of each flask to 100 ml and set aside for 10 min. Prepare, simultaneously with the other solutions, a control solution containing no fluoride.

Measure the optical density (0·02–0·52) of the fluoride solutions against the cerium^{III}-alizarin complexanate control at 610 mμ in 4-cm cuvettes. The curve is linear from 5–35 μg, but falls off only very slightly at 50 μg.

Procedure (B): 50–500 μg *of fluoride ion* (620 mμ).

Pipette 1–10-ml aliquots of a 50 μg/ml fluoride solution into 100-ml standard flasks, add 10 ml of $5 \times 10^{-3}M$ alizarin complexan solution and 4 ml of buffer solution (pH 5·0–5·2) from pipettes to each flask, followed by 10 ml of $5 \times 10^{-3}M$ cerium^{III} solution with constant swirling of the contents of the flask during the addition of the latter. Dilute the contents of each flask to 100 ml and set aside for 90 min. Prepare, simultaneously with the other solutions, a control containing no fluoride.

Measure the optical density (0·027–0·32) of the fluoride solutions against the cerium^{III}-alizarin complexanate control at 620 mμ in 2-mm cuvettes. The curve is linear from 50–275 μg and falls off only slightly at 400 μg.

Procedure (C): 100–1000 μg *of fluoride ion* (620 mμ).

Pipette 1–10-ml aliquots of a 100 μg/ml fluoride solution into 100-ml standard flasks, add 25 ml of $5 \times 10^{-3}M$ alizarin complexan solution and 5 ml of buffer solution (pH 5·0–5·2) from pipettes to each flask, followed by 25 ml of $5 \times 10^{-3}M$ cerium^{III} solution, then proceed as in (*B*).

Measure the optical density (0·04–0·66) as above at 620 mμ in 2-mm cuvettes. The curve is linear from 100–550 μg and falls off only slightly at 800 μg.

Procedure (D): 200–1600 μg *of fluoride ion* (630 mμ).

Pipette 2–16-ml aliquots of a 100 μg/ml fluoride solution into 100-ml flasks, add 25 ml of $10^{-2}M$ alizarin complexan solution and 10 ml of buffer solution (pH 5·0–5·2) from pipettes to each flask, followed by 25 ml of $10^{-2}M$ cerium^{III} solution, then proceed as in (*B*).

Measure the optical density (0·134–1·085) as above at 630 mμ in 2-mm cuvettes. The curve is linear from 200–800 μg.

Elimination of interference

(a) *Masking procedures:* Pipette 10 ml of $2{\cdot}6 \times 10^{-3}M$ sodium fluoride solution into a 100-ml flask followed by 1 ml of a $2{\cdot}6 \times 10^{-2}M$ solution of the appropriate cation. Wash down the walls of the flask and allow to stand for 30 min. Add 1 ml of the appropriate masking agent and allow to stand for 5 min. Then apply *Procedure* (*C*) as usual.

(b) *Extraction procedure:* Pipette 10 ml of $2{\cdot}6 \times 10^{-3}M$ sodium fluoride solution into a 100-ml flask followed by 1 ml of a $2{\cdot}6 \times 10^{-2}M$ solution of the appropriate cation. Wash down the walls of the flask and allow to stand for 30–60 min. Add 5 ml of buffer solution (pH 5·0–5·2) followed by 1 ml 2·26% of 8-hydroxyquinoline solution. Some metals may be extracted almost immediately but with others, *e.g.* aluminium, it is best to allow precipitation to occur over the next 1·5–2 hr.

Extract the solution with three equal phase volumes of chloroform. Wash the combined chloroform extracts once with a half-phase volume of distilled water and add the washing to the original aqueous phase. Add 25 ml each of $5 \times 10^{-3}M$ alizarin complexan solution and, with constant swirling, $5 \times 10^{-3}M$ cerium^{III} nitrate solution. Dilute to 250 ml and develop the colour in the usual way for 90 min or overnight. Measure at 620 mμ in a 2-mm cuvette.

It is not necessary in the masking procedures to carry the reference cerium^{III}-alizarin complexanate solution through the same process, but it is advisable to do so in order to cater for impurities or small variations in experimental parameters such as pH. Standard fluoride solutions passed through the extraction process in the absence of foreign metal ions showed no significant increase or decrease in optical density.

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Note: In all applications of the method it is important always to add the buffer solution and alizarin complexan solution before the cerium[III] solution.

Zusammenfassung—Der optimale pH-Bereich der Cer(III)-Alizarinkomplexanatmethode zur Bestimmung von Fluoride wurde zu 5–5·2 ermittelt. 5 μg (0·1 ppm) bis zu 1·6 mg (160 ppm) Fluorion können mit einem üblichen Spektrophotometer bestimmt werden. Einfluss des pH-Wertes auf die Färbung sowie die Störungen durch 23 Kationen und 3 Anionen werden diskutiert Fast alle Kationenstörungen können durch Maskierung ausgeschaltet werden. Nur in airigen, wenigen Fällon ist vorherige Extraktion mit Oxin in Chlorform nötig.

Résumé—Le domaine de pH le plus convenable pour le dosage du fluorure par la méthode du complexe cérium(III)-alizarine est 5–5,2; à cette valeur de pH la méthode peut être appliquée dans un grand domaine de concentration: de 5 μg de fluorure (0,1 ppm) à 1,6 mg (160 ppm) en utilisant un spectrophotomètre ordinaire. La nature des changements produits dans le système coloré par variation du pH est brièvement discutée et l'interférence de 23 cations et de 3 anions ordinaires a été interprétée. Pratiquement l'interférence de tous les cations importants peut être surmontée par simple addition d'un agent complexant, mais dans certains cas une extraction préliminaire par la 8-hydroxyquinoléine et le chloroforme est nécessaire.

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A COMPARATIVE STUDY OF SOME LANTHANON CHELATES OF ALIZARIN COMPLEXAN AS REAGENTS FOR FLUORIDE

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Summary—A study has been made of the comparative suitability of the cerium^{III}, lanthanum and praseodymium chelates of alizarin complexan as reagents for the spectrophotometric determination of microgram amounts of fluoride. The cerium^{III} reagent is most sensitive at pH $< 4{\cdot}5$ and the lanthanum reagent at pH $> 5{\cdot}0$. An enhancement of sensitivity may be obtained for both reagents at pH 4·3 by addition of acetone to 25% v/v, but the most sensitive means of determination is to use the lanthanum reagent in aqueous solution at pH 5·2 with measurement at 281 mμ. This procedure is 200% more sensitive than the standard method at 620 mμ.

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LEONARD and West[1] have previously observed that fluoride ion forms soluble blue coloured ternary complexes with the red alizarin complexan chelates of the first few elements of the lanthanon series, *viz.* lanthanum, cerium^{III} and praseodymium. The fourth and fifth members of the series, neodymium and promethium, were not available but the ensuing rare earth, samarium, showed only slight colour formation and subsequent members showed no colour formation at all. At pH 4·3, the cerium^{III} reagent was found to be more sensitive than the others.

It has since been suggested[2] that the lanthanum reagent has advantages over the cerium^{III} reagent on the grounds of sensitivity, but comparative data have been

TABLE I. DIFFERENCE IN OPTICAL DENSITIES BETWEEN ALIZARIN COMPLEXAN CHELATES AND THEIR TERNARY FLUORIDE COMPLEXES

Wavelength of measurement, mμ	Difference in optical densities $\times 10^3$						
	pH 4·3				pH 5·7		
	Ce	La	Pr	Sm	Ce	La	Pr
590	186	171	147	19	174		35
600	194	172	152	13	174	182	40
610	199	173	161	6	200	207	50
620	188	165	152		204	210	52
630	160	135	128		178	184	42

lacking. In the present paper comparative studies have been made and a more sensitive procedure has been developed.

Reagents based on lanthanum, cerium^{III} and praseodymium were compared at pH 4·3 and 5·7 in sodium acetate buffers under carefully controlled conditions. The results shown in Table 1 were obtained with solutions containing 5×10^{-6} of a mole each of alizarin complexan, the lanthanon nitrate and sodium fluoride in a total volume of 100 ml. The lanthanon solutions were prepared from "Specpure" materials

and their stock solutions were standardised against EDTA using Xylenol Orange as indicator at pH 5·1, before dilution. These results indicate clearly that at pH 4·3, when interferences with the method are likely to be less than at higher pH values, the cerium^{III} reagent is slightly superior to those based on lanthanum and praseodymium. In all three cases the maximum sensitivity towards fluoride occurs at 610 mμ. The samarium-based reagent develops only a slight colour with fluoride and the maximum absorption occurs at 590 mμ. A gadolinium based reagent similarly formulated showed no optical activity whatsoever towards fluoride ion under these conditions. At pH 5·7 all three reagents showed maximum sensitivity towards fluoride ion at 620 mμ. It would appear that at this pH the ternary praseodymium complex is partly hydrolysed as there is a marked fall in absorption. There is a slight enhancement for cerium^{III}, but it is considerably more marked with the lanthanum reagent which at this pH is slightly (*ca.* 3%) more sensitive than the cerium^{III} reagent under the same conditions.

Comparison of lanthanum and cerium^{III} reagents over pH range 4·3–5·9

A narrower pH range was studied by preparing calibration curves (5–50 μg) for fluoride ion based on 1:1 lanthanum and cerium^{III} chelates of alizarin complexan. Repeated check experiments revealed that at pH 4·3 (610 mμ) the cerium^{III} reagent was, as reported previously,[1] slightly more sensitive than the reagent based on lanthanum. At pH 4·5 (610 mμ) the difference in sensitivity between the two reagents becomes vanishingly small. At pH 5·1 (620 mμ) the lanthanum based reagent is approximately 4% more sensitive than the cerium^{III} reagent and this slight advantage is maintained at pH 5·5 and pH 5·9. At both of these pH values there is, however, a decrease in sensitivity for lanthanum as well as for cerium^{III}.

Enhancement of sensitivity

It has previously been reported that the ternary complex between cerium^{III}, alizarin complexan and fluoride ion may be extracted from aqueous solution with a non-miscible organic solvent.[1] In this process an enhancement of sensitivity is obtained. The enhancement, apart from the concentration factor, may be caused by the effect of lower dielectric constant favouring association of the complex and replacement of the co-ordinated water molecule still attached to the cerium^{III} ion in the ternary complex.[1] Accordingly, the effect of the addition of miscible solvents was examined because it was expected that a similar enhancement would result.

Four suitable solvents, two alcohols, one ketone and an ether were examined at pH 4·3, all at the same concentration (20% v/v). The results of this examination, shown in Table II, indicate the superiority (under the specified conditions) of acetone with its sterically unhindered keto-oxygen atom, relatively high basicity and low dielectric constant. Despite the basicity of its oxygen atoms, dioxan is nearly as effective as ethanol, presumably because of its lower dielectric constant. Similarly, methanol is less effective than the other solvents.

The cerium^{III} and lanthanum reagents were next compared in a 20% acetone medium and their performance was checked against variation of pH. This series of experiments revealed that acetone had a more pronounced effect on the lanthanum reagent. The optimum sensitivity in a 20% acetone medium was obtained at pH 4·3 and the wavelength of maximum difference shifted from 610 to 620 mμ. Under the

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TABLE II. EFFECT OF SOLVENTS ON THE SENSITIVITY OF THE LANTHANUM METHOD
5×10^{-6} MOLE OF LANTHANUM CHELATE + 25 μg OF F^-/100 ml.

Wavelength of measurement, $m\mu$	Optical density $\times 10^3$											
	Methanol			Ethanol			Acetone			Dioxan		
	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity
600	178	289	111	134	280	146	159	312	153	110	250	140
610	155	274	119	107	265	158	124	301	177	85	244	159
620	123	247	124	77	237	160	91	267	176	60	222	162
630	096	210	114	51	193	142	61	215	154	38	183	145

TABLE III. EFFECT OF ACETONE CONCENTRATION ON SENSITIVITY OF LANTHANUM REAGENT. 5×10^{-6} MOLE OF LANTHANUM CHELATE + 25 μg OF F^-/100 ml

Acetone, %	Optical densities (at 620 mμ) $\times 10^3$		
	Lanthanum chelate	Fluoride complex	Sensitivity
10	70	220	150
15	92	265	173
20	111	296	177
25	136	316	180
30	153	327	174
35	170	334	164

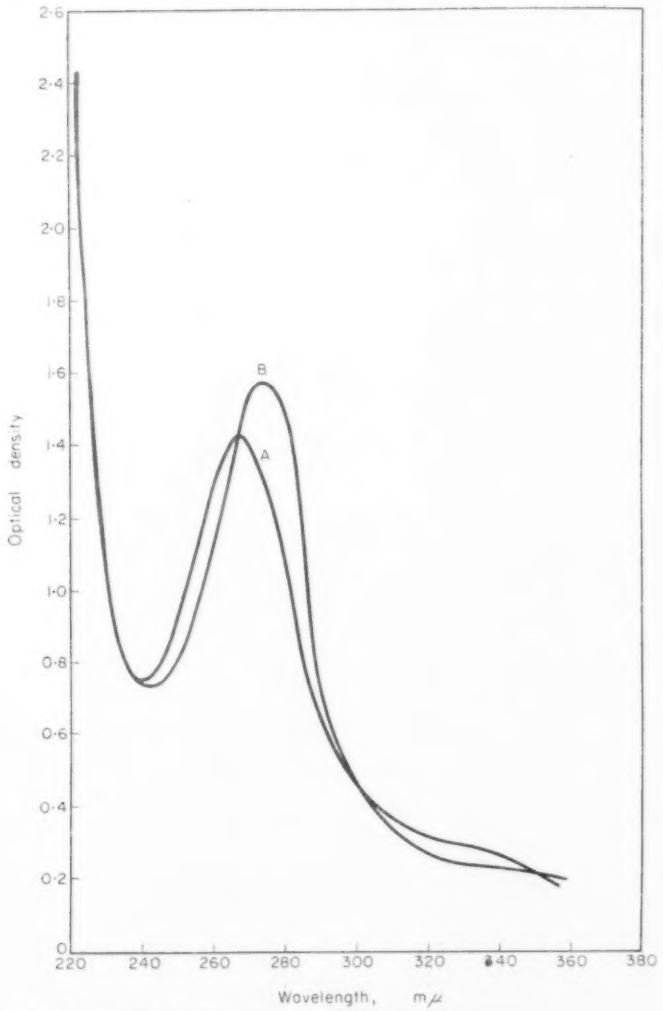

FIG. 1.—Absorption curves for cerium based reagent.
A—5×10^{-6} Mole of cerium chelate in 100 ml of solution, pH 5·2.
B—5×10^{-6} Mole of ternary fluoride complex in 100 ml of solution, pH 5·2.
10-mm light path, measured against water.

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optimum conditions the lanthanum reagent was *ca.* 3% more sensitive than the cerium reagent and 20% more sensitive than the lanthanum reaction in aqueous solution at the same pH. The "apparent" pH of these acetone solutions measured on a pH meter was 4·68.

Finally, in this series of experiments, the optimum concentration of acetone was

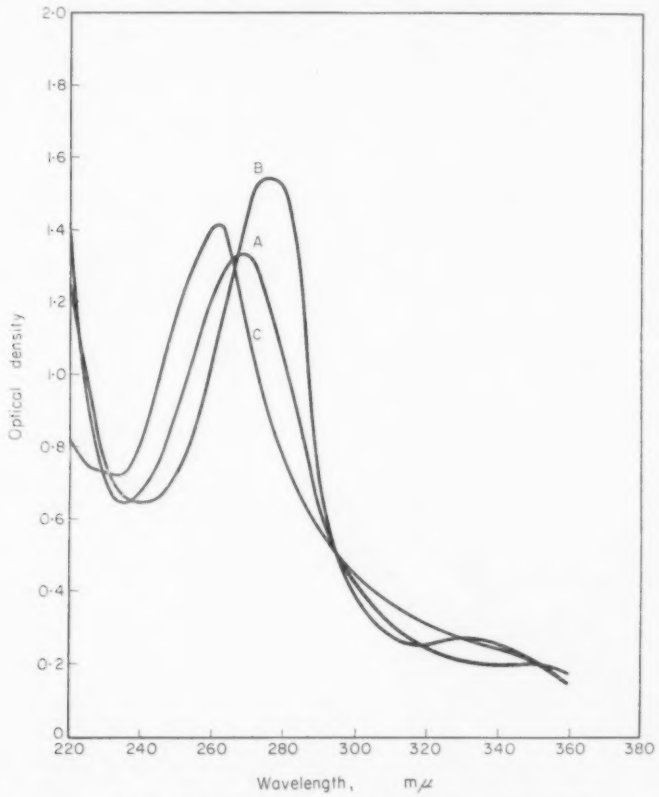

FIG. 2.—Absorption curves for lanthanum based reagent.
A—5 × 10^{-6} Mole of lanthanum chelate in 100 ml of solution, pH 5·2.
B—5 × 10^{-6} Mole of ternary fluoride complex in 100 ml of solution, pH 5·2.
C—5 × 10^{-6} Mole of alizarin complexan in 100 ml of solution, pH 5·2.

established for the lanthanum based reagent at pH 4·3. The results of this investigation are summarised in Table III and show clearly that the optimum concentration is 25%.

Absorption in the ultra-violet region

An examination of the mechanism of the fluoride reaction previously proposed by Leonard and West[1] and observation of absorption spectra of the chelate and ternary complex published in previous papers[1,3] suggests that one would expect to get considerable absorption in the ultraviolet region. Accordingly, the ultraviolet spectra of the exactly formulated 1:1 chelates and 1:1:1 complexes for cerium^{III} (Fig. 1) and lanthanum (Fig. 2) were plotted. These reveal that there is a much stronger absorption

in the ultraviolet region and at the wavelength of maximum sensitivity (281 mμ) the lanthanum method is slightly more sensitive (*ca.* 8%) than the cerium^{III} method. At the optimum pH of 5·0–5·2 the sensitivity of the lanthanum procedure is 200% greater at 281 mμ than at 620 mμ.

Fig. 3 shows a series of calibration curves drawn up for the lanthanum reagent at

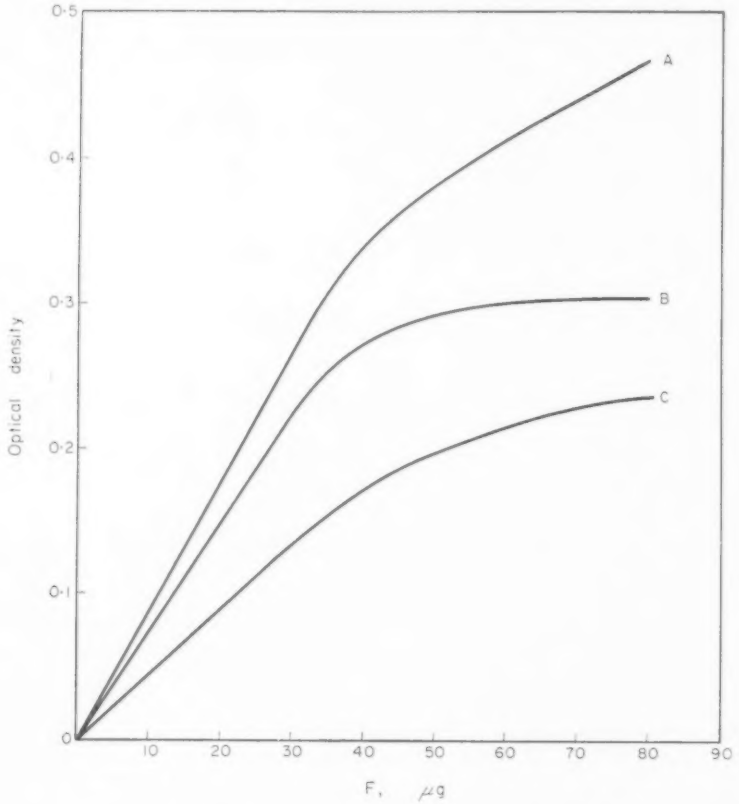

FIG. 3.—Calibration curves for lanthanum reagent.
A—5 × 10^{-6} mole of lanthanum chelate in 100 ml of solution, pH 5·2, 5–100 μg of fluoride, 10-mm silica cell at 281 mμ.
B—5 × 10^{-6} mole lanthanum chelate in 100 ml of 25% acetone solution, pH 4·3, 5–100 μg of fluoride, 10-mm glass cell at 620 mμ.
C—As A, but using 10-mm glass cell at 620 mμ.

pH 5·2 in aqueous solution at 620 and 281 mμ and at 620 mμ and pH 4·3 in a 25% acetone medium. This last curve flattens out much more markedly than those for the aqueous solutions beyond the upper level of the curve where the Lambert-Beer law is obeyed. It is noticeable also that the projection of these lanthanum curves passes through the origin.

CONCLUSION

The optimum sensitivity of the alizarin complexan method for fluoride is obtained with a lanthanum based reagent operated in aqueous solution at pH 5·0–5·2 with

measurements of optical density at 281 mμ. Under these conditions the reaction is 200% more sensitive than that previously reported.[3] Below pH 4·5 the cerium^{III} reagent is slightly more sensitive than the lanthanum reagent. Both are superior to a reagent based on the praseodymium chelate.

EXPERIMENTAL

Reagents

$5 \times 10^{-4}M$ *Solutions of cerium*^{III}, *lanthanum and praseodymium nitrates*: Prepared by dilution from accurately standardised (EDTA, pH 5·2, Xylenol Orange) 0·02M solutions made from "Specpure" materials (Johnson and Matthey).

$5 \times 10^{-4}M$ *Alizarin complexan solution*: *cf.* Reference 3.

Buffer solution (pH 5·0–5·2): 100 g of AnalaR sodium acetate trihydrate + 11 ml of glacial acetic acid dissolved in distilled water and diluted to 1 litre.

Standard fluoride solution: 5 μg of F^-/ml, *cf.* Reference 3.

Apparatus

Hilger "Uvispek" Spectrophotometer, 1-cm silica and glass cells.

Preparation of calibration curves

(A) *Aqueous solution* (620 mμ) *and* (281 mμ): Pipette 10 ml of $5 \times 10^{-4}M$ alizarin complexan solution into a 100-ml graduated flask, then add 2 ml of buffer solution (pH 5·0–5·2) and 1–10 ml of standard fluoride solution. Finally, add, with constant swirling of the contents of the flask, 10 ml of $5 \times 10^{-4}M$ lanthanum nitrate solution and dilute to the mark. Prepare similarly a control solution containing all of the reagents but no fluoride. Set the solutions aside for at least 1·5 hr and measure the optical density of the fluoride solutions in 10-mm cells [silica for 281 mμ, 1 mm slit; glass for 620 mμ, 0·05 mm slit] against the control solution.

(B) 25% *Acetone solution*: As above, but use 2 ml of buffer solution (pH 4·3) and add 25 ml of acetone after the addition of the lanthanum solution.

Analyses of unknowns

Take an aliquot of solution containing from 5–35 μg (5–30 μg for 25% acetone experiments) of fluoride in not more than 78 ml of solution and carry through the above procedure (A).

Note: For routine analytical work it is not necessary to use "Specpure" salts. Normal lanthanum nitrate hexahydrate may be used, but it must be standardised against EDTA, since the composition of the salt may be variable.

Acknowledgement—We are grateful to the Department of Scientific and Industrial Research for the provision of the Hilger and Watts "Uvispek" spectrophotometer used in this study.

Zusammenfassung—Die Eignung der Alizarinkomplexanchelate von Cer(III), Lanthan und Praseodym zur photometrischen Bestimmung von Mikrogrammengen Fluors wird verglichen. Das Cer(III) reagens zeigt höchste Empfindlichkeit bei pH-Werten unterhalb von 4·5 während das Lanthanreagens pH 5·0 oder höher verlangt. Ein Anstieg der Empfindlichkeit für beide Reagenzien wird beobachtet wenn bei pH 4·3 in 25 volumperzentiger Acetonlösung gearbeitet wird. Die höchste Empfindlichkeit wird mit dem Lanthanreagens erzielt bei pH 5·2 in wässriger Lödung unter Messen bei 28i mμ. Diese Variante ist 200 mal empfindlicher als die Standardmethode bei 620 mμ.

Résume—Les auteurs ont étudié la valeur comparative des chelates du cérium(III), du lanthane et du praséodyme avec l'alizarine comme réactifs pour le dosage spectrophotométrique de quantités de fluorure de l'ordre du microgramme. Le réactif avec le cérium(III) est sensible à pH $<$4,5 et celui avec le lanthane à pH $>$5,0. On peut augmenter la sensibilité des deux réactifs à pH 4,3 par addition d'acétone à 25%, mais la méthode de dosage la plus sensible est l'utilisation du réactif contenant le lanthane en solution aqueuse à pH 5,2 avec mesure à 281 mμ. Cette méthode est deux fois plus sensible que la méthode standard à 620 mμ.

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INFRARED CORRELATIONS IN THE BILE ACID SERIES

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Summary—The infrared spectra of a number of esters and free acids in the cholanic acid series have been examined with the aid of a special solvent system which overcomes the problem of solubility. Eleven absorption regions in the 9–12 μ region have been correlated with specific substitution on the steroid nucleus and side chain. In certain cases, perturbations were found when di- or tri-substitution occurred in rings A, B, and/or C.

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INTRODUCTION

THE "finger-print" region of the infrared spectra of steroids (7–15 μ) has been of great use in characterisation of the stereochemistry of the A/B ring junction as well as of the substitution on the steroid nucleus. Œstrogens,[1] progesterones,[2] cholesterol derivatives,[3] as well as ketones,[4] alcohols,[5] and esters[6] have been examined in this region with the purpose of correlating specific absorptions with particular functional groups in the molecule. Usually mono-functional compounds were examined because of the perturbations caused by different groups in polyfunctional compounds. Some studies indicated that satisfactory correlations may be obtained only when the substituted groups were widely separated in the molecule, as is found in 3,17- or 3,20-difunctional compounds.[6,7]

The bile acid series of compounds has not been examined extensively. One deterrent has been the difficulty in dissolving these compounds in solvents suitable for infrared investigation. The polarity of the poly-hydroxylated acids, as well as their methyl esters makes it difficult using normal cell thickness to prepare solutions concentrated enough for examination of the inherently weak absorptions found in the "finger-print" region.

As noted by Ard and Fontaine,[8] however, normally insoluble acids may be dissolved in infrared-suitable solvents if a small amount of basic compound, such as triethylamine, is also present. This innovation led to the formulation of a solvent system sufficiently transparent in the 6-6·5 μ and 9-12 μ regions. This system was used in the examination and correlation of certain specific group absorptions of mono-, di-, and tri-substituted bile acid compounds in these regions.

EXPERIMENTAL

The compounds examined and their sources are listed in Table I. The parent compound, cholanic acid, is shown in Fig. 1. Most substitution was at the 3, 7, and/or 12 positions. Chromatography, specific colour reactions, melting points, and lack of spectral change after recrystallisation were used as purification criteria. Purity was estimated to be at least 95% in all cases. Some compounds were demonstrated to be at least 99% pure by chromatographic techniques. Reagents used were reagent-grade except where noted otherwise.

* Deceased 3 *June* 1960.

TABLE I. COMPOUNDS EXAMINED AND THEIR SOURCES

1.	Methyl cholanate	(a,b)*
2.	Methyl lithocholate (3-hydroxy)	(a,c)
3.	Methyl deoxy-cholate (3,12-dihydroxy)	(a,c)
4.	Methyl chenodeoxy-cholate (3,7-dihydroxy)	(a,c)
5.	Methyl hyodeoxy-cholate (3,6-dihydroxy)	(a,c)
6.	Methyl cholate (3,7,12-trihydroxy)	(a,c)
7.	Methyl 3-hydroxy-7-acetoxy-cholanate	(d)
8.	Methyl 3-hydroxy-12-acetoxy-cholanate	(d)
9.	Methyl 3-hydroxy-7,12-diacetoxy-cholanate	(d)
10.	Methyl 3,7-diacetoxy-12-hydroxy-cholanate	(e)
11.	Methyl 3-hydroxy-7-acetoxy-12-keto-cholanate	(e)
12.	Methyl 3,12-dihydroxy-7-acetoxy-cholanate	(e)
13.	Methyl 3,7,12-triacetoxy-cholanate	(f)
14.	Methyl 3-keto-7-acetoxy-cholanate	(d)
15.	Methyl 3-keto-12-acetoxy-cholanate	(d)
16.	Methyl 3,7-diacetoxy-12-keto-cholanate	(e)
17.	Methyl 3-keto-7,12-diacetoxy-cholanate	(d)
18.	Methyl dehydrocholate (3,7,12-triketo)	(a,c)
19.	Cholanic acid	(b)
20.	Lithocholic acid (3-hydroxy)	(c)
21.	7-Hydroxy-cholanic acid	(g)
22.	12-Hydroxy-cholanic acid	(d)
23.	Deoxy-cholic acid (3,12-dihydroxy-)	(c)
24.	Glycodeoxy-cholic acid	(h)
25.	Chenodeoxy-cholic acid (3,7-dihydroxy-)	(e)
26.	Glycochenodeoxycholic acid	(i)
27.	7,12-Dihydroxy-cholanic acid	(d)
28.	Hyodeoxy-cholic acid (3,6-dihydroxy)	(c)
29.	Cholic acid (3,7,12-trihydroxy)	(c)
30.	Glycocholic acid	(j)
31.	3-Hydroxy-7-keto-cholanic acid	(k)
32.	3-Hydroxy-12-keto-cholanic acid	(e)
33.	3,7-Dihydroxy-12-keto-cholanic acid	(e)
34.	3-Acetoxy-cholanic acid	(f)
35.	3,6-Diacetoxy-cholanic acid	(f)
36.	3,7-Diacetoxy-cholanic acid	(f)
37.	3,12-Diacetoxy-cholanic acid	(f)
38.	3,7,12-Triacetoxy-cholanic acid	(f)
39.	3-Keto-cholanic acid	(a)
40.	3,7-Diketo-cholanic acid	(a)
41.	3,12-Diketo-cholanic acid	(a)
42.	Dehydrocholic acid (3,7,12-triketo)	(c)
43.	Δ^4,3-Keto bis nor cholenic acid	(c)
44.	Stearic acid	(d)

*a. *Biochem. J.*, 1954, **55,** 292.
b. *J. Amer. Chem. Soc.*, 1949, **71,** 3301.
c. Commercial.
d. *Biochem. J.*, 1944, **38,** 108.
e. *J. Amer. Chem. Soc.*, 1950, **72,** 5530.
f. *Analyt. Chem.*, 1959, **31,** 1808.
g. *Biochem. J.*, 1946, **40,** 52.
h. *J. Biol. Chem.*, 1936, **113,** 779.
i. *Arkiv. Kemi*, 1955, **8,** 331.
j. *J. Amer. Chem. Soc.*, 1935, **57,** 1393.
k. *Biochem. J.*, 1954, **56,** 581.

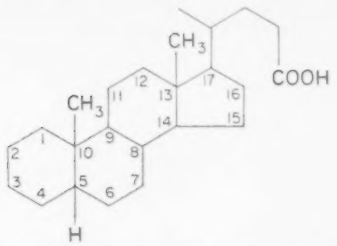

FIG. 1.—Structural formula of cholanic acid.

By evaporation of an aliquot of an alcoholic standard solution at 110°, 0·01 to 0·02 millimoles of bile acid compound were placed in a 1- or 2-ml glass-stoppered volumetric flask. A fresh solution of 2% triethylamine (Matheson) in bromoform (Baker's "Purified") was prepared, and 0·3 ml was added to the cooled steroid residue in the flask, which was then stoppered and shaken to dissolve the compound. The infrared spectra were obtained on a Perkin-Elmer Infracord-137 instrument. The sample cell in all cases was 0·468 mm in thickness, and was scanned with a reference cell (0·467 mm) containing the 2% triethylamine solvent. Calibration spectra were run periodically, and corrections were made on the steroid spectra when necessary. The wavelength accuracy was estimated to be within $\pm 0{\cdot}02\ \mu$ as determined by a calibrating polystyrene strip. Fresh solvent was prepared with each series of approximately 10 spectra, and the reference solution was changed for each compound. The results shown in Table II do not necessarily indicate all the absorption bands found in the 9–12 μ region; rather they indicate those absorptions where some degree of correlation is possible.

RESULTS AND DISCUSSION

Table II shows the wavelength and apparent molar absorptivities in the correlated regions. Absence of results indicates that the absorption in the specified region could not be differentiated from the background absorption at the concentrations used. Inflections have not been noted; obvious shoulders on the sides of strong absorption bands are, however, included. Usual background absorptivities were in the range of 10–30 units. Tentative assignments of various functional group absorptions are shown in Table III.

Because reaction of the acidic solute with the basic solvent usually increased the background absorption, a base-line technique was used to calculate absorbances and molar absorptivities. In all cases a straight line parallel to the 100% transmittance line was drawn through the absorption at 5·4 μ, which was the point of minimum absorption in most of the spectra. The absorbance of the compound was then calculated by subtracting the base-line absorbance from the absorbance indicated by the spectrum. The apparent molar absorptivities were calculated from the following formula:

$$a_M = A(MW)/c(d),$$

where A = absorbance, MW = molecular weight, c = concentration in mg/ml, and d = thickness in cm.

Anomalies in spectra of compounds in potassium bromide pellets have been noted by other investigators.[9,10,11] This has been shown to be particularly true with compounds containing hydroxyl groups.[12] For this reason it was decided that for the most reproducible results, solution techniques were necessary.

Ard and Fontaine[8] indicated that if 1–2·5% solutions of triethylamine in either carbon disulphide or carbon tetrachloride were used to dissolve acids for infrared sampling, the neutralisation of the acid by the base could cause some change in the

TABLE II. ABSORPTION BANDS

	6·25 μ and 9–10 μ bands						10–11 μ bands*			
Compound	6·25	9·32	9·65	9·71	9·78	9·89	10·22	10·32	10·56	10·65
1			9·65s† (48)			9·88 (60)			10·60 (19)	
2				9·72 (144)		9·88 (93)			10·58 (36)	
3			9·65 (261)			9·87 (107)		10·32 (47)	10·56 (63)	
4		9·33 (172)‡		9·70 (94)		9·87 (84)	10·22 (183)			
5				9·72 (294)						
6		9·31 (177)	9·64 (190)			9·85s (106)	10·21 (138)		10·54 (71)	
7		9·35 (132)		9·72s (138)	9·82 (181)			10·33 (124)		10·64 (61)
8				9·70 (324)	9·70 (324)	9·86s (160)¶		10·32 (112)	10·53 (43)	
9		9·35 (153)		9·72s (280)	9·80 (281)	9·85s (280)¶		10·32 (137)		10·66 (56)
10		9·40 (137)	9·64s (222)		9·77 (346)			10·33 (101)		10·64 (88)
11		9·35s (134)		9·73s (190)	9·80 (196)			10·31 (107)		10·66 (65)
12		9·35 (185)	9·66 (226)	9·73s (220)	9·80s (215)			10·30 (119)		10·63 (77)
13		9·35s (102)			9·78 (455)			10·35 (137)		10·65 (74)
14			9·58 (96)		9·82 (146)			10·31 (72)		10·65 (63)
15			9·58s (75)		9·75 (175)			10·32 (103)		
16		9·41 (101)			9·78 (299)			10·32 (98)		10·65 (78)
17			9·56s (100)		9·78 (228)			10·32 (101)		10·65 (58)
18			9·68 (67)			9·91 (67)				
19	164‡		9·68 (69)						10·58 (81)	
20	169			9·72 (208)					10·60 (65)	
21	172			9·70 (75)		9·91 (106)	10·22 (75)		10·59 (51)	
22	182		9·65 (116)			9·91 (63)			10·6–·7 (53)	
23	175		9·65 (302)			9·88 (107)		10·33 (63)	10·59 (109)	
24	280s		9·64 (314)			9·88 (121)		10·31 (53)	10·58 (88)	
25	165	9·32 (153)		9·71 (112)		9·90 (76)	10·23 (180)			
26	232s	9·32 (153)		9·71 (111)		9·89 (65)	10·23 (165)			
27	181		9·68 (134)	9·72 (134)			10·20 (77)		10·53 (60)	
28	164			9·73 (285)						
29	174	9·32 (174)	9·64 (216)			9·86s (98)	10·22 (135)		10·53 (85)	
30	282s	9·32 (181)	9·64 (224)			9·87s (108)	10·22 (119)		10·53 (62)	
31	178	9·33 (103)	9·6–·7 (98)	9·6–·7 (98)		9·91 (103)	10·25 (98)			
32	170			9·71 (246)			10·22 (80)			
33	162	9·32 (146)	9·6–·7 (123)	9·6–·7 (123)		9·86s (84)		10·33 (84)		
34	172				9·76 (215)		10·22 (86)		10·54 (54)	
35	183				9·76 (428)		10·22 (101)			
36	165	9·41 (101)			9·79 (288)			10·34 (122)		10·64 (86)
37	168				9·75 (358)			10·30 (76)		
38	182	9·35s (75)			9·78 (450)			10·35 (86)		10·65 (93)
39	195		9·6–·7 (65)	9·6–·7 (65)		9·88s (41)			10·59 (50)	
40	172		9·6–·7 (47)	9·6–·7 (47)		9·91s (42)				
41	184		9·6–·7 (75)	9·6–·7 (75)		9·90s (62)			10·53 (57)	
42	135		9·6–·7 (73)	9·6–·7 (73)		9·91 (70)				
43	185s		9·6–·7 (56)	9·6–·7 (56)						
44	157		9·6–·7 (58)	9·6–·7 (58)						

* See text for correlation of 11·6 and 12·0 μ bands.
† s-Shoulder.
‡ Apparent molar absorptivity.
¶ Approximate.

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TABLE III. SUMMARY OF TENTATIVE SPECTRAL CORRELATIONS

Wavelength, μ	Functional group
6·25	Carboxylate ion (170)*
9·32	3,7-Bifunctional compounds (145)
	All acids (50)
9·65	12-Hydroxyl group (222)
	Ketones (70)
	All compounds (60)
9·71	3-Hydroxyl and 7-hydroxyl groups (see text)
	General (see text)
9·78	Mono-acetates (188)
	Di-acetates (314)
	Tri-acetates (453)
9·89	Most 3-hydroxy compounds without 7-hydroxyl group (106)
	General (85)
10·22	7-Hydroxyl group (134)
10·32	Acetates (107)
10·56	12-Hydroxy group (74)
	Many others
10·65	7-acetates (72)
11·65	Methyl esters (30)
12·0	Acids (80)

* Average apparent molar absorptivity

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spectra and give rise to some absorption bands not otherwise present. In order to study more fully the effect of solvent composition on solubility of the bile acid compounds, as well as the effects on the spectra obtained, a series of mixtures was prepared using varying percentages of triethylamine in different solvents. Compounds dissolved in 1% and 2% triethylamine solutions of the same solvent yielded essentially the same spectra although some of the compounds were less soluble in the 1% solution. When the concentration of triethylamine was increased to 3%, the absorption band of the amine at 9·1 μ became intense enough to render the region from 9·0–9·3 μ less useful. It was therefore decided to use a 2% solution of triethylamine in a suitable solvent for further investigations. In 0·3 ml of this solvent there is approximately 0·05 millimole of base, approximately three times the amount of steroid involved, so that an adequate excess is provided for complete neutralisation of free acids. Carbon tetrachloride and carbon disulphide, even with added triethylamine, were not capable of dissolving some of the hydroxylated compounds, even when warmed. The use of methylene chloride, bromodichloromethane, dibromochloromethane, and trichloroethylene was investigated, but it was found that either they had poor solvent power or they obscured large regions of the "finger-print" region. Chloroform possessed the solvent properties, but had intense absorptions in the 9–12 μ range. Bromoform, however, was quite transparent in this spectral range, and had good solvent properties for all the compounds investigated, and a 2% triethylamine solution was used for this study. The following is a discussion of each of the correlated regions—

6·25 μ: It has been noted that upon neutralisation of carboxylic acids, the absorption at 5·75 μ disappears to be replaced by two strong bands at longer wavelengths.[13] The basicity of triethylamine in the solvent caused this neutralisation of free acids,

and the carboxylate ion bands appear at 6·25 and 7·2 μ. No absorption is found in the carbonyl region if compounds containing only carboxyl and hydroxyl groups are dissolved in this basic solvent. Obviously ketones and esters will yield intense carbonyl absorptions if present. This technique therefore is a rapid method for detecting the presence of carbonyl groups in carboxylic acids without resorting to the preparation of derivatives. As indicated in Table II, all the carboxylic acids yield relatively intense absorptions in the 6·25 μ region. Apart from the three glycine conjugates (24, 26, 30) and the Δ^4, 3-keto compound (44), which, because of other strong bands in the region, do not yield a separate band for the carboxylate group, the average molar absorptivity, irrespective of other functional groups present, is 171 litre mole^{-1} cm^{-1} with an average deviation of 8 units.

9·32 μ: Absorption in this region is indicative of the simultaneous presence of carbon-oxygen bonds at carbons-3 and -7. As shown in Table II, compounds having hydroxyl groups at both positions (4,6,25,26,29,30,33) have strong absorption bands in the 9·31–9·33 μ range. Compounds which contain the 3-hydroxyl and 7-acetoxy groups simultaneously have the absorption shifted to 9·35 μ (7,9,11,12). Compounds having acetoxy groups at both the 3 and 7 positions (10,16,13,36) have the absorption shifted to still longer wavelengths, at 9·40–9·41 μ. The two tri-acetoxy compounds (13,38) also have absorptions shifted to longer wavelengths, although the band is found as a shoulder on the side of the very intense acetate absorption band at 9·8 μ. 3-Hydroxy-7-keto-cholanic acid (31), the only 3-hydroxy-7-keto compound studied, also has a reasonably strong absorption band at 9·33 μ. It is probable that as the hydroxyl groups are acetylated, the absorption band is shifted progressively to longer wavelengths, although the absorptivity remains about the same, the average for the seventeen compounds being 144 litre mole^{-1} cm^{-1}. All free acids examined also have a small absorption band in this region. However, the absorptivity is always less than 50 units and is easily differentiated from the much more intense 3,7-bifunctional vibration.

9·65 μ: All compounds were found to have some absorption in the order of 50–70 units in this region, although it was rather diffuse, and precise wavelengths could not be assigned. All ketones were also found to have rather general absorption from 9·6–9·8 μ with absorptivities ranging from 50–100 units. The strong, sharp absorption of the 12-hydroxy compounds (3,10,6,12,22,23,24,27,29,30) from 9·64–9·68 μ, however, was readily apparent and easily differentiated from the more diffuse absorption. Apart from 12-hydroxy- and 7,12-dihydroxy-cholanic acids (22,27), the molar absorptivities of these compounds range between 190 and 314 units. Apparently the presence of substitution at carbon-3 enhances the 12-hydroxyl group vibration.

9·71 μ: As noted in the previous section, all compounds have weak absorption in this region, especially the ketones, the absorptivities generally being less than 70 units. It is apparent from Table II that all compounds with either a 3-hydroxyl or a 7-hydroxyl group also have intense absorption in this region. The three cholate compounds have this region obscured by the strong 12-hydroxyl vibration at 9·65 μ. The 7-hydroxyl group absorption itself is comparatively weak as indicated in 7-hydroxy- and 7,12-dihydroxy cholanic acids (21,27); even when a hydroxyl group is also present at carbon-3, the average molar absorptivity is about 110 units (4,25,26,33). On the other hand, the ten 3-hydroxy compounds with no hydroxyl group at carbon-7

have an average molar absorptivity of 223. This would seem to indicate that the simultaneous presence of the hydroxyl group at carbon-7 decreases the absorption from 3-hydroxyl groups. The infrared absorption of the 3-hydroxy compounds with no other substitution in rings A, B, or C has been studied and this structure was found to absorb at a slightly longer wavelength than found in this study.[5,7] This is apparently caused by the differences in polarity of the solvents used.

9·78 μ: Acetate groups are characterised by having relatively intense absorption bands in this region. Molar absorptivities range from 146–455 for mono-, di-, and tri-acetates. 3-Acetates have also been examined by other investigators and found to have absorption in this region.[6,14] The presence of keto groups seems to depress the absorption of the acetate group in most cases. The molar absorptivity of methyl-3,7-diacetoxy-12-keto-cholanate (16) is 14% less than that of methyl-3,7-diacetoxy-cholanate (10). It is 19% less in the case of methyl-3-keto-7-acetoxy-cholanate (14) and methyl-3-hydroxy-7-acetoxy-cholanate (7). There is also a 19% decrease in the case of methyl-3-keto-7,12-diacetoxy-cholanate (17) and methyl-3-hydroxy-7, 12-diacetoxy-cholanate (9). The 86% increase in the absorptivity of methyl-3-hydroxy-12-acetoxy-cholanate (8) as compared with methyl-3-keto-12-acetoxy-cholanate (15) probably arises from the overlapping of the 3-hydroxyl absorption at 9·70 μ with the acetate absorption at 9·75 μ, which causes one strong band to occur at 9·70 μ. Except for this compound, mono-acetates have absorptivities of 146–215 with an average of 188 units. Diacetates have a range of 228–428 units with an average of 314, and the two tri-acetates have an average of 453 units. From these results it appears that the introduction of each acetoxy group, whether substituted at the 3, 7, or 12 position, increases the absorptivity approximately 130 units.

9·89 μ: Almost all compounds containing acetate groups have this region obscured by the intense absorption at 9·75 μ. Two acetates, however, methyl-3-hydroxy-12-acetoxy-, and 3-hydroxy-7,12-diacetoxy-cholanate (8,9), have shoulders on the side of the acetate band, but accurate determination of absorptivities was not possible. Of the remaining compounds, almost all show some absorption in this region, ketones and most of the 7-hydroxy compounds having absorptivities less than 85 units. Compounds containing a 3-hydroxyl group have increased absorption, with absorptivities ranging from 93–121 units, the average for nine compounds being 106.

10·22 μ: Absorption in this region is characteristic of all 7-hydroxy compounds. However, the six compounds which also contain a 3-hydroxyl group (4,6,25,26,29,30) have an average molar absorptivity twice that of 7-hydroxy- and 7,12-dihydroxy-cholanic acids (21,27). The marked enhancement apparently arises from the interaction of the 3- and 7-hydroxyl group vibrations. The only exception to this correlation is 3,7-dihydroxy-12-keto-cholanic acid (33), although it has an uncorrelated and unexplained band at 10·33 μ. Also having absorptions in this region are 3-hydroxy-7-keto- and 3-hydroxy-12-keto-cholanic acids (31,32), although no other 3-hydroxy compounds have similar absorptions except those also containing the 7-hydroxyl group. Two acetates, 3-acetoxy-, and 3,6-diacetoxy-cholanic acids (34,35), also have absorption in this region. These bands, however, are probably the acetate absorptions shifted down from 10·33 μ (see next section).

10·32 μ: Absorption in this region is characteristic of acetate groups on the steroid molecule. Fourteen acetoxy compounds have molar absorptivities ranging

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from 76–137 units with an average of 107. The only acetoxy compounds examined which showed no absorption were 3-acetoxy- and 3,6-diacetoxy-cholanic acids (34,35). However, both of these compounds have unexplained absorption bands of similar intensities at 10·22 μ which are probably due to shifting of the 10·32 μ band. The three deoxy-cholic acid compounds (23,24,33) also have bands in this region, although the absorptivities are significantly lower. The only other compound absorbing in this region is 3,7-dihydroxy-12-keto-cholanic acid. This may be the 7-hydroxyl group band that should appear at approximately 10·23 μ but is shifted because of the presence of the 12-keto group.

10·56 μ: Correlation in this region is less definite than the preceding ones. All 12-hydroxy compounds (3,6,22,23,24,27,29,30) have intensities of 53–109 units except for two compounds (10,12) which have this region obscured by strong absorption at 10·63 μ. Many other compounds, however, have significant absorption in this region, as indicated in Table II, and still others show inflections on the sides of other strong bands. No final correlation could be made.

10·65μ: All 7-acetoxy compounds have absorption in this region, molar absorptivities ranging from 56–93 units, with an average of 72 for the ten compounds. No other compounds absorbed in this region.

Miscellaneous absorptions: All methyl esters examined have an absorption band at 11·6–11·7 μ with absorptivities between 15 and 40 units. Also, all acids have absorption at 11·98–12·03 μ, the majority of the absorptivities falling between 75 and 85 units. Although these absorptions are relatively weak, they are readily

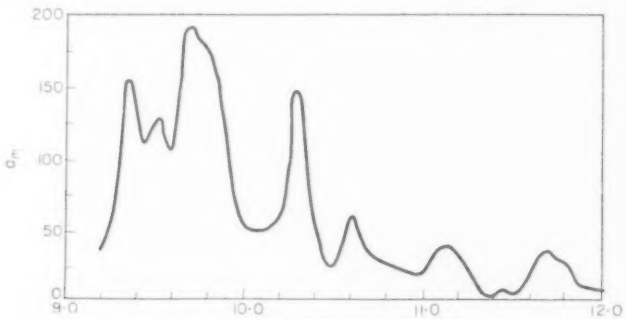

FIG. 2.—Summation spectrum.

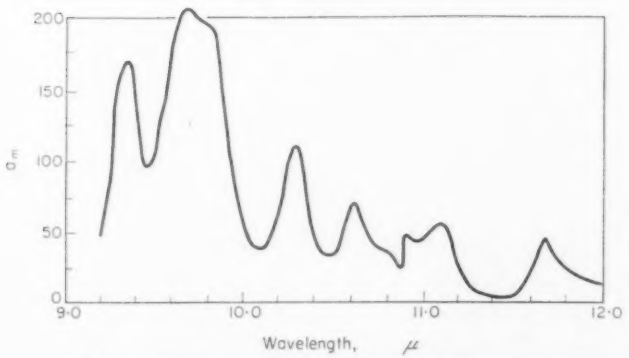

FIG. 3.—Spectrum of methyl-3-hydroxy-7-acetoxy-cholanate.

apparent in the spectra of the compounds. Differentiation between the spectra of free acids and their methyl esters is easily made by examination of these two regions. Except for these bands, the spectra of the free acids and their methyl esters in the 9–12 μ range were indistinguishable.

Summation spectra: Although some studies have indicated the possibility of preparing summation spectra of complex molecules by using the absorptivities of simpler molecules, the preparation has not been attempted with steroids with functional groups in close proximity.[6,7] This attempt has been made in the present study. Fig. 2 illustrates the summation spectrum produced by adding the apparent molar absorptivities of methyl 3-hydroxy-7-acetoxy-cholanate (7) and 12-hydroxy-cholanic acid (22) and subtracting the values of cholanic acid (19). This should yield the spectrum of methyl-3,12-dihydroxy-7-acetoxy-cholanate (12), shown in Fig. 3. It is evident that these spectra are quite similar in spite of the presence of substitution in rings A, B, and C. This indicates the possibility of preparing summation spectra of more complex molecules. However, certain combinations of functional groups such as found in 3,7-dihydroxy compounds make this difficult because of perturbations.

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Zusammenfassung—Die Infrarotspektren einer Anzahl von Estern und freien Säuren der Cholansäurereihe wurden untersucht, wobei ein besonderes Solventsystem verwendet wurde um die Lösungsschwierigkeiten zu beheben. Elf Absorptionsbereiche zwischen 9 und 12 μ wurden spezifischen Substituenten im Steroidkern und der Seitenkette zugeordnet. In bestimmten Fällen wurden Störungen beobachtet, wenn Di- oder Trisubstitution in den Ringen A, B und/oder C auftrat.

Résumé—Les spectres infra-rouge d'un certain nombre d'esters et d'acides libres dans la série de l'acide cholanique ont été examinés grâce à un solvant spécial qui résout le problème de la solubilité. Onze domaines d'absorption dans la région 9–12 μ ont été reliés à la substitution spécifique sur le noyau stéroïde et la chaîne latérale. Dans certains cas, les auteurs ont trouvé des perturbations quand une di ou une trisubstitution se produisait dans les cycles A, B et/ou C.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—VIII*

THIOGLYCOLLIC ACID AS A MASKING AGENT

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Summary—The masking properties of thioglycollic acid (TGA) as well as the possibilities of its use in complexometry have been studied. It has been found that thioglycollic acid in an alkaline medium perfectly masks metals such as Pb, Bi, Cd, Ag, Hg, Zn, Tl, In and Sn because of the formation of colourless complexes. In this medium TGA forms intensely coloured complexes with Fe, Co and Ni. The red coloration of the Fe-TGA complex can be prevented by the addition of triethanolamine. It has been found that the Ni- and Co-EDTA complexes do not react with TGA. This enables a highly selective determination of nickel and cobalt to be made. Also, manganese can be determined in the presence of other metals screened with TGA. The advantages of TGA in comparison with potassium cyanide are discussed.

POTASSIUM cyanide is still a frequently used masking agent in complexometry, because it permits the direct complexometric determination of calcium and magnesium even in the presence of some divalent metals forming sufficiently stable complex cyanides. In view of its extreme toxicity, however, it ranks among the less popular reagents, particularly in routine analysis. In many countries its storage and consumption are under the control of various safety regulations so that large quantities of it in laboratories are not much favoured. Its replacement by an equally efficient, non-toxic and inexpensive reagent is desirable.

Some time ago certain substances were proposed to meet this emergency. Thus one can mention 2,3-dimercaptopropanol[1] which, however, on account of its price, was not introduced to any appreciable extent. Our experiments have revealed that of a number of substances the properties of which recommend them for use in complexometry, thioglycollic acid (TGA) is the most advantageous. Its main asset, compared with potassium cyanide, is the fact that in an alkaline medium it also forms colourless and soluble complexes with a number of other metals such as lead, bismuth, tin, *etc.* Further advantages are that it can be safely added even to acidic solutions and that, in using its neutralised solutions, the pH of the titrated solution is not essentially changed. In aqueous solutions it is sufficiently stable.

In masking of the accompanying cations the colour of the complexes formed is always of great significance. Although thioglycollic acid is well known as a sensitive colorimetric reagent for iron, with which it forms in an alkaline medium an intense red complex, a judicious choice of conditions (the presence of triethanolamine and sodium hydroxide) also makes it applicable to the masking of other elements even in the presence of iron. Like cyanide, it forms a colourless complex with copper in an alkaline medium.

* Part VII: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1961, **8**, 743.

TABLE I. REACTIONS OF THIOGLYCOLLIC ACID

Ion	Remarks
Ag	A yellow-white, gelatinous precipitate, insoluble in an excess of TGA, readily soluble in ammonia. Ammoniacal TGA also dissolves AgCN and AgI.
Hg	A white precipitate soluble in mineral acids and ammonia to give a colourless solution. The Hg-EDTA complex also reacts quantitatively with TGA.
Bi	A yellow-white precipitate, soluble in an excess of TGA as well as in ammonia to give a colourless solution. The Bi-EDTA complex reacts quantitatively with TGA both in an acidic and alkaline medium.
Cd	A white precipitate, soluble in an excess of reagent or in ammonia to give a colourless solution. Similar properties are observed with the Cd-EDTA complex.
Pb	A white yellow precipitate, soluble in ammonia. The EDTA complex reacts quantitatively also with TGA. $PbSO_4$ and $PbCrO_4$ are soluble in ammoniacal TGA.
Cu	First a brown solution, then a precipitate, changing on addition of further TGA to a yellow one, soluble in ammonia to give a colourless solution. The Cu-EDTA complex behaves similarly.
Tl	Masked in an acidic as well as alkaline medium. In acidic solution at higher concentrations of Tl a crystalline precipitate, soluble in ammonia, separates. The EDTA complex reacts similarly. (Possibility of determination of Th in the presence of Tl in an acidic medium-Xylenol Orange as indicator).
As, Sb	Without marked colour reactions.
Sn	A colourless complex in an alkaline medium.
Fe	In an acidic medium, a reduction, producing an unstable blue coloration, occurs first. Subsequently the solution becomes colourless, then turns intensely red on the addition of ammonia. In the presence of triethanolamine (TEA) and sodium hydroxide the solution is decolourised because of the formation of a TEA-complex. The Fe-EDTA complex is slowly reduced by TGA.
Cr, Al, Ti Th, Be	Without marked colour reaction.
Ni	The brown coloration developed in an alkaline medium disappears on the addition of EDTA. The Ni-EDTA complex does not react with TGA. (Possibility of determination of Ni in the presence of Cu, Zn, Cd, *etc.*)
Co	The yellow-brown to red-brown coloration developed in an alkaline medium does not change on the addition of EDTA. (Possibility of masking small amounts of Co in the determination of Ni.) The Co-EDTA complex does not react with TGA. (Possibility of determination of Co in the presence of Pb, Cu, Zn, *etc.*.)
Mn	No reaction in an acidic medium. In an alkaline medium an unstable brown-yellow coloration develops, deeping on stirring and in contact with air. The addition of KCN produces an intense red coloration, becoming paler on standing but deepening on stirring and in contact with air. The presence of ascorbic acid gives no colour response. The Mn-EDTA complex does not react with TGA. (Possibility of determination of Mn even in the presence of TGA.)
Zn	A colourless complex in an alkaline medium. Perfect masking against EDTA.
In	A colourless complex in an alkaline medium. Also, the In-EDTA complex reacts with TGA.
Ga	Does not react with TGA at all. (Possibility of determination of Ga besides In.)
WO_4^{2-}	A slightly yellow coloration in an acidic medium even in the presence of EDTA. In an alkaline medium the coloration disappears.
MoO_4^{2-}	An intense yellow coloration in an acidic medium even in the presence of EDTA. In an alkaline medium the coloration disappears.
UO_2^{2+}	An intense red coloration in an alkaline medium even in the presence of EDTA.
Ca, Sr, Ba, Mg	Without colour reactions.

The study of the reactions of thioglycollic acid with metal ions in the presence of EDTA or DCTA (1,2-diaminocyclohexan-N,N,N′,N′-tetra-acetic acid) has revealed still further advantages over potassium cyanide. For example, the EDTA complex with nickel or cobalt does not react in an alkaline medium with TGA, which permits a number of further, hitherto impracticable complexometric determinations, such as that of nickel in the presence of copper, zinc, iron, *etc.*, to be made. This preliminary communication presents a survey of the reactions of TGA with currently occurring cations with respect to the requirements of complexometry, and gives examples of some new determinations.

EXPERIMENTAL

Reagents

A 16% solution of thioglycollic acid was prepared from an 80% solution (produced by Lachema, Brno) by dilution with redistilled water (1:5). The solutions of the cations and of EDTA and DCTA were prepared in 0·05*M* concentrations from reagent-grade chemicals.

Orientation experiments

The orientation experiments, the results of which are presented in Table I, were carried out as follows: 5 to 10 ml of a 0·05*M* solution of the corresponding cation were diluted to about 50 ml, TGA added in portions and the changes in the solution observed. Subsequent to this the solution was neutralised with conc. ammonia solution and 20 ml added in excess. The same procedure was applied to reactions proceeding in the presence of an excess of EDTA and of DCTA.

A similar study has been made of the reactions of cations in the presence of DCTA, which, as is known, forms more stable complexes than does EDTA. As would be anticipated some DCTA complexes reacted with TGA only very slowly or not at all. Accordingly, the use of DCTA in combination with TGA is not recommended.

TABLE II. DETERMINATION OF Ni IN THE PRESENCE OF Cu, Cd, Pb, Zn AND Ag

Ni taken, *mg*	Other metal(s) taken, *mg*	0·05*M* EDTA, *ml*	0·05*M* $CaCl_2$, *ml*	Ni found, *mg*
14·26		10·00	5·14	14·26
14·26	(thioglycollic acid)	10·00	5·17	14·18
14·26	3·18 Cu	10·00	5·17	14·18
14·26	63·54 Cu	10·00	5·12	14·32
14·26	127·08 Cu	10·00	5·12	14·32
14·26	28·10 Cd	10·00	5·13	14·29
14·26	56·20 Cd	10·00	5·17	14·18
14·26	140·51 Cd	10·00	5·05	14·52
14·26	51·80 Pb	10·00	5·17	14·18
14·26	518·03 Pb	10·00	5·21	14·07
14·26	16·35 Zn	10·00	5·12	14·32
14·26	163·50 Zn	10·00	5·17	14·18
14·26	53·94 Ag	10·00	5·14	14·26
14·26	539·40 Ag	10·00	5·15	14·22
57·04	31·77 Cu, 28·10 Cd, 51·80 Pb 65·38 Zn	25·00	5·55	57·09
57·04	15·88 Cu, 28·10 Cd, 51·80 Pb 16·35 Zn, 269·50 Ag	25·00	5·55	57·09
57·04	15·88 Cu, 28·10 Cd, 51·80 Pb 65·38 Zn	25·00	5·52	57·15
5·70	31·77 Cu, 56·20 Cd, 103·60 Pb, 32·69 Zn, 107·88 Ag	10·00	7·95	5·96

Selective determination of nickel

As one of many cases presented in the above survey of reactions of TGA the possibility of the indirect determination of nickel in the presence of a number of elements has been studied. The procedure is based on a back-titration of an added excess of EDTA with calcium solution, to a Thymolphthalexone end-point.

Procedure: To an acidic solution of the cations (see Table II), TGA (1:5) is added in small portions or dropwise. This is accompanied by various colour changes depending on the composition of the solution. In the absence of copper the coloration is pure brown because of the formation of the Ni-TGA complex. If copper is present, there is a transient brown colour. With further addition of TGA a yellow precipitate appears. On the addition of 20 to 25 ml of conc. ammonia solution the precipitate dissolves and only the brown Ni-TGA complex remains. A slight excess of 0·05*M* EDTA solution decolorises it, the solution then being faintly blue because of the formation of the Ni-EDTA complex. The solution is diluted when necessary, Thymolphthalexone added and the excess of EDTA back titrated with 0·05*M* calcium chloride solution to an intensely blue coloration. Some results for this procedure are given in Table II.

Out of the other interfering elements the most likely to be encountered are aluminium and iron. The masking of aluminium by means of triethanolamine presents no difficulties. Iron, if the solution is not extremely alkaline, reacts with TGA to give an intense red coloration. However, if sufficient sodium hydroxide is now added, the solution becomes decolorised completely or remains only slightly yellow. This is because the increased alkalinity produces a quantitative formation of the Fe-TEA complex which does not interfere in the determination. Another advantage of TEA is that it prevents the separation of nickel hydroxide in the strongly alkaline medium.

For the determination of nickel in the presence of iron the above described procedure must be somewhat modified: To an acidic solution of nickel, copper, iron, aluminium and other heavy metals, add thioglycollic acid (1:5), in portions, to the disappearance of the brown coloration and to the formation of a bright yellow precipitate (Cu-TGA salt). On the addition of 20 ml of 20% triethanolamine the solution turns intensely red (Fe-TGA complex). Add 1*M* sodium hydroxide till the red coloration completely disappears (Fe-TEA complex). Now add a small excess of 0·05*M* EDTA solution and allow to stand for 3–5 min with occasional stirring. At this point the solution is generally too alkaline and it is, therefore, advisable to dilute it to 300–350 ml to eliminate interference from the bluish colour of the Ni-EDTA complex in the colour change of the indicator. The excess EDTA is titrated, as in the foregoing case, with 0·05*M* calcium chloride solution to an intense blue end-point using Thymolphthalexone as indicator. Some of the results are presented in Table III.

TABLE III. DETERMINATION OF Ni IN THE PRESENCE OF Fe, Cu AND Al

Ni taken, *mg*	Other metal(s) taken, *mg*			Ni found, *mg*
	Fe	Cu	Al	
2·85	13·97	317·7	13·49	2·93
28·52	2·79	15·89	13·49	28·78
28·52	13·97	158·85	26·98	28·69
14·26	2·79	158·85	13·49	14·28
14·26	8·38	158·85	13·49	14·36
14·26	13·97	15·89	26·98	14·35
57·04	8·38	158·85	13·49	57·23
57·04	27·93	317·70	—	58·54[a]

[a] End-point not sharp.

In a parallel study of the analysis of iron-chromium-nickel alloys[2] we have found that for a strongly alkaline medium the most suitable indicator is Fluorexon (calcein). The above described method can, therefore, be modified as follows: After making the solution alkaline with potassium hydroxide (not with sodium hydroxide[3]), add Fluorexon solution dropwise till the faintly blue solution turns pink, then titrate with calcium chloride solution to the appearance of a distinct green fluorescence. In this case the end-point is much sharper than with Thymolphthalexone.

Selective determination of manganese

Like nickel, manganese can also be determined if retained in the bivalent state by means of ascorbic acid (hydroxylamine hydrochloride is not sufficiently efficient in this case). The procedure is the same as the proceeding one, except that 0·1–0·2 g of ascorbic acid is initially added to the solution to be analysed. Several results of the determination of manganese in the presence of other metals are given in Table IV.

TABLE IV. DETERMINATION OF Mn IN THE PRESENCE OF Fe, Cu AND Al

Mn taken, *mg*	Other metal(s) taken, *mg*			Mn found, *mg*
	Fe	Cu	Al	
5·39	13·97	15·89	6·75	5·38
13·47	13·97	158·85	13·49	13·56
26·95	2·79	31·77	26·98	27·01
53·89	13·97	317·70	6·75	53·90

Zusammenfassung—Die Maskierungseigenschaften von Thioglycollsäure (TGS) und ihr möglicher Gebrauch in der Komplexometrie wurden studiert. Es wurde gefunden, dass TGS unter Bildung farbloser Komplexe die nachfolgenden Elemente in alkalischem Medium vollständig maskiert: Pb, Bi, Cd, Ag, Hg, Zn, Tl, In und Sn. In alkalischem Medium werden intensiv gefärbte Komplexe von Fe, Cu und Ni gebildet. Die Bildung des roten Eisenkomplexes kann durch Zusatz von Triäthanolamin verhindert werden. Die ÄDTE-komplexe von Ni und Co reagieren nicht mit TGS, was eine hochselektive Bestimmung der beiden Metalle ermöglicht. Mangan kann in Gegenwart anderer Metalle bestimmt werden, wenn letztere mit TGS maskiert sind. Die Vorteile von TGS gegenüber Kaliumcyanid werden diskutiert.

Résumé—Les auteurs ont étudié les propriétés complexantes de l'acide thioglycollique (TGA), ainsi que les possibilités de son utilisation en complexométrie. Ils ont trouvé que l'acide thioglycollique dissimule complètement en milieu alcalin des métaux comme Pb, Bi, Cd, Ag, Hg, Zn, Tl, In, Sn par formation de complexes incolores. Dans ce milieu, le TGA forme des complexes colorés de facon intense avec le fer, le cobalt et le nickel. La coloration rouge du complexe Fe-TGA peut être évitée par addition de triéthanolamine. Par la suite, les auteurs ont trouvé que les complexes Ni-EDTA et Co-EDTA ne réagissent pas avec le TGA. Celà permet un dosage extrêmement sélectif du nickel et du cobalt. Le manganèse peut aussi être dosé en présence d'autres métaux complexés par le TGA. L'avantage du TGA par rapport au cyanure de potassium a été discuté.

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PHOTOMETRIC TITRATIONS—V*

A SELECTIVE, CHELOMETRIC DETERMINATION OF COBALT

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Summary—Cobalt can be titrated with good selectivity by converting it with hydrogen peroxide in alkaline medium to the cobalt^{III} EDTA complex and back-titrating photometrically in acid medium the excess EDTA with bismuth solution, using pyrocatechol violet as indicator. No interference is observed with alkalies, alkaline earths, Ni, Cu, Cd, Zn, Pb, Al, U, and W. Bi, Zr, In, Ga and other ions forming very stable EDTA complexes are co-titrated. Mo, Fe, Ag and Hg interfere and should be separated. The interference of Mn can be excluded by addition of ascorbic acid. Th can be masked with sulphate. Cr^{III} is co-titrated, but by applying a difference method operating with two aliquots, both Cr and Co can be determined. Complexing anions interfere, as does chloride, which causes a turbidity with bismuth.

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A PARTICULAR chelometric determination of cobalt using the element in its tervalent state has been described by Kinnunen and Wennerstrand.[1] Cobalt in ammoniacal solution is oxidised with hydrogen peroxide in the presence of EDTA. The solution is then acidified to pH 2 and the excess of EDTA is back-titrated with standard thorium solution using xylenol orange as indicator. Only small amounts of cobalt can be titrated using this procedure because the very intense red colour of the cobalt^{III} EDTA complex readily obscures the end-point. A photometric end-point should improve the method considerably. Thorium, however, is not the best choice for the back-titration, for several reasons, and the present authors have investigated the use of bismuth for this purpose employing pyrocatechol violet as indicator.

This titration is possible even at very low pH values,[2] where most of the other metals do not react with the indicator and where the apparent stability constants of their EDTA complexes are so low that the metal ions are readily replaced by bismuth. The replacement reaction, however, is slow in some cases (nickel and to some extent copper); hence it is better to complex with bismuth the EDTA which is in excess over the cobalt, thus hastening the replacement, and then to titrate the excess bismuth with EDTA. There is no danger that any cobalt^{III} might be replaced, even after prolonged standing with excess bismuth, because the $Co^{III}Y$ complex was estimated to have a very high stability constant ($\log K = 40{\cdot}7$).[3] Back-titrations with bismuth have successfully been used for the determination of various metal ions,[4] and the method was especially useful for a selective visual titration of nickel where nickel was frozen in the EDTA complex by lowering the temperature of the solution to nearly 0°.[5]

Photometric determination of the end-point

The absorbance curves of pyrocatechol violet and its bismuth complex at various pH values are shown in Fig. 1. From these curves it can be deduced that even at pH 0·5 a sufficient difference between the absorbances of the two species exists at a

* Part III—*Talanta*, 1961, **8**, 720.

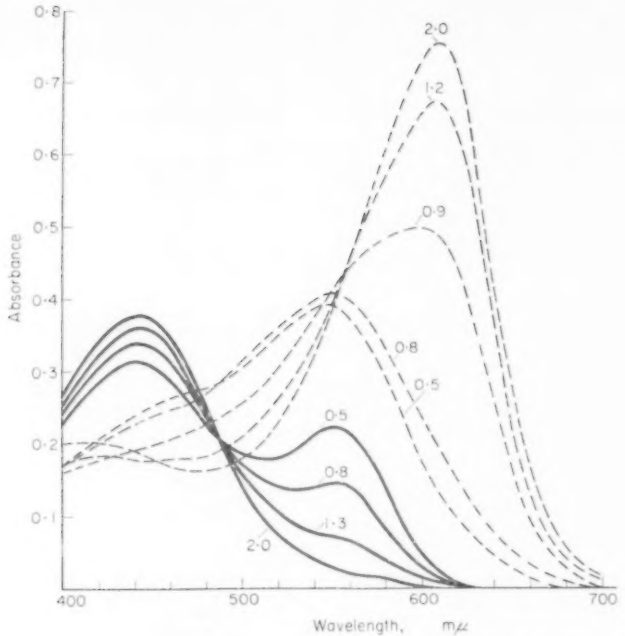

FIG. 1.—Absorbance curves of pyrocatechol violet (solid line) and its bismuth complexes (dotted line) at various pH values.

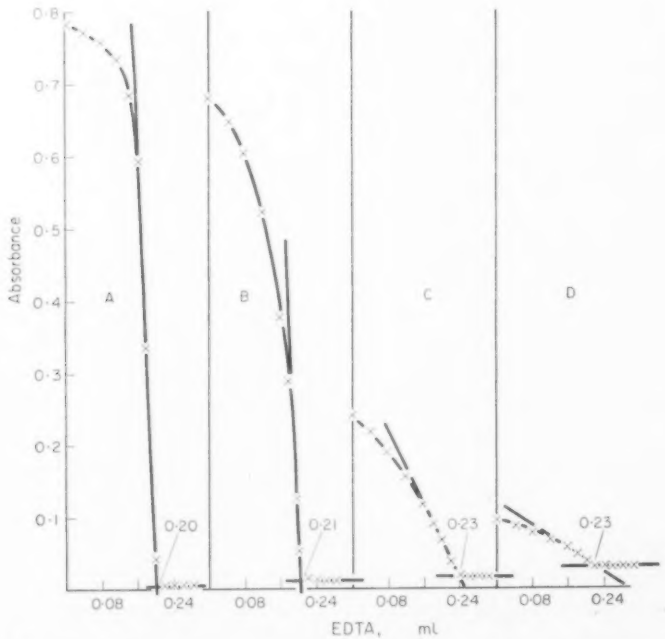

FIG. 2.—Photometric titration curves near the end-point of bismuth with EDTA, using pyrocatechol violet as indicator at various pH values. Curves A to D are for pH 2·0, 1·5, 1·0 and 0·5 respectively.

wavelength of about 600 to 620 mμ to provide the condition for a suitable photometric end-point. Experimental determination of the titration curves at various pH values are shown in Fig. 2. The precision is within the limits to be expected.

The cobalt^{III} EDTA complex

It is known that there are two red complexes, which do not appear very different in colour to the eye, but which may be distinguished by a phototitrator. The cobalt-EDTA complexes have been studied by Schwarzenbach.[6] In alkaline medium the oxidation of the cobalt^{II}-EDTA complex by hydrogen peroxide proceeds, according to Schwarzenbach, in the following manner:

$$\underset{\text{pinkish}}{2\ CoY^{2-}} + H_2O_2 \rightarrow 2\ \underset{\text{deep blue}}{Co(OH)Y^{-2}} \qquad (1)$$

On acidification a proton is attached, this process being accompanied by a colour-change to red:

$$\underset{\text{deep blue}}{Co(OH)Y^{2-}} + H^+ \rightarrow \underset{\text{red}}{Co(H_2O)Y^-} \qquad (2)$$

The complex containing one molecule of co-ordinated water is not stable, and it dissociates in a rather slow process according to the equation

$$\underset{\text{red}}{Co(H_2O)Y^-} \rightarrow CoY^- + \underset{\text{red}}{H_2O} \qquad (3)$$

The absorbance curves of both complexes are shown in Fig. 3. Fortunately the two curves are identical at the wavelength selected for the titration, hence there will be no interference from this process.

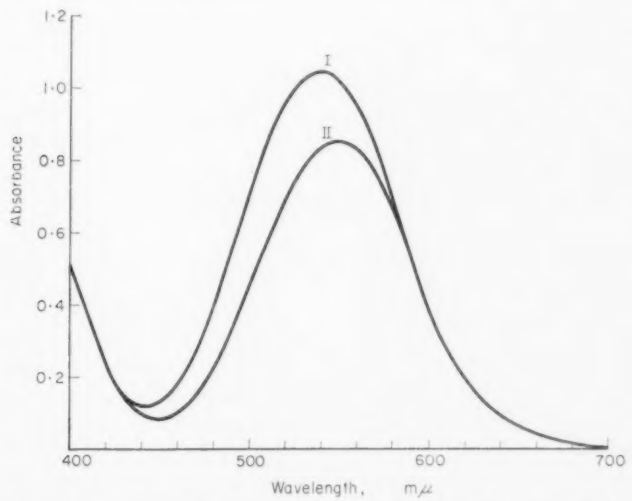

FIG. 3.—Absorbance curves of the complexes $Co(H_2O)Y^-$ (I) and CoY^- (II) at pH about 1·8.

Kinnunen and Wennerstrand[1] performed the cobalt oxidation in an ammoniacal medium. This, however, has been found to be inconvenient for the present purpose because the hydrogen peroxide oxidises the ammonia to nitrogen. This results in

the formation of a large number of small bubbles which are difficult to remove, and which can interfere with the response of the photititrator. The solution was therefore made basic with sodium hydroxide solution. A smaller amount of oxidant suffices for complete oxidation of the cobalt, and barely any bubbles are produced. In addition, the rate of the oxidation reaction seems to be greatly enhanced. In consequence of these findings it seems to be more realistic to write reaction (1) in a modified form involving the hydroxo complex of the cobalt^{II} EDTA. In alkaline medium above pH 10 the colour is no longer the clear pink of the complex CoY^{-2} as present in neutral solution.

A study of the oxidation mechanism revealed that only the cobalt^{II} which is complexed by EDTA is rapidly oxidised. Hence the addition of EDTA which represents an excess with respect only to the amount of cobalt present is not adequate when other metal ions are present (except alkali metals). A partial replacement of cobalt^{II} may occur according to the equation

$$CoY^{-2} + M^{n+} \rightleftarrows MY^{n-4} + Co^{2+} \qquad (4)$$

How far this equilibrium will be shifted towards the right depends on the concentration of M and on the ratio of the stability constants of the complexes involved. Even with a metal like magnesium, which has a low stability constant, the shift is sufficient to cause low results in the cobalt determination when a portion of the magnesium remains uncomplexed.

EXPERIMENTAL

The photititrator described in a previous paper of this series was used.[7] The titrations were performed in rectangular cells having a 1·5- and 3-cm lightpath and 100- or 200-ml capacity. An interference filter, 622 mμ, was used. Metal and EDTA solutions were prepared from reagent-grade material and standardised according to well established chelometric procedures. The absorbance curves were made with a Cary Model 14 Recording Spectrophotometer. An approximately 0·2% aqueous solution of pyrocatechol violet was used.

Procedure

Add a measured amount of standard EDTA solution to the sample so that all metal ions present (except the alkalies) are complexed and some EDTA is present in excess. Add 2*N* sodium hydroxide solution dropwise while stirring until a pH of about 11 is reached. Add 4–5 drops of 30% hydrogen peroxide and stir. Add concentrated nitric acid dropwise, until the desired pH is reached (0·5–2) depending on the composition of the sample. Add a spatula-tip full of urea and stir. Add several drops of indicator solution (more than would be used for a visual end-point) and adjust the titrator so that about 90% T is read.*

Add an exactly measured amount of bismuth standard solution at least equivalent to the EDTA present. Titrate the free bismuth with standard EDTA. Near the end-point add small increments of titrant only. Plot ml of titrant on the abscissa (linear) and transmittance readings on the ordinate (logarithmic) using semilog paper. Evaluate the graph to find the end-point in the usual manner.

Calculation: Let A be the total number of ml of EDTA added (before the oxidation step and during the final titration), and B the ml of bismuth solution added. Then the calculation is based on the following formula, where M is the molarity of the solution indicated by the subscript:

$$(A \times M_{EDTA} - B \times M_{Bi}) \times 58{\cdot}94 = \text{mg of cobalt.}$$

Study of interferences

No interference was observed through oxidation of EDTA by the moderate amounts of unreacted hydrogen peroxide at pH 10–11. Similarly at pH 0·5 no reaction

* Adjustment to 100% T is not recommended because sometimes the final transmittance reading is higher than the initial one. Thus the above procedure provides some sort of a safety range.

was noticeable; at least not during the time required to complete the analysis. Even in the presence of considerable amounts of ascorbic acid the cobalt^{III} EDTA complex is not reduced in acid medium. It is known[2] that the oxides of nitrogen present in nitric acid will react with pyrocatechol violet, thus causing a very rapid drift of the galvanometer. Hydrogen peroxide left over from the oxidation step oxidises the nitrogen oxides and thus eliminates the interference; it does not attack the indicator. Urea serves equally well for eliminating this kind of interference.

The oxidation of cobalt^{II} EDTA is slower at pH < 10. Hence it is important that the pH be adjusted to a value greater than 10 so that complete oxidation is assured without undue prolongation of the procedure.

The following ions do not interfere at a pH of 2 or lower: alkalies, alkaline earths, Ni, Cu, Zn, Cd, Pb, and UO_2^{+2}.

Aluminium is only very slowly and incompletely replaced at pH 2 but no interference occurs at pH 0·5–0·7. Thus cobalt may be titrated in the presence of these elements without any masking procedures.

Manganese is also oxidised to an $Mn^{III}Y$ complex which interferes. The complex, however, can readily be reduced by ascorbic acid. It is important to add this reductant after acidification of the oxidised solution and just before the addition of the indicator.

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If the solution containing chromium^{III} and cobalt is treated according to the normal procedure chromium interferes. Results for cobalt determinations are found to be high, indicating that some of the chromium is being co-titrated. Chromium forms its EDTA complex very slowly, so that it is precipitated during the alkalinisation step. Some of the chromium is converted to chromate when hydrogen peroxide is added to the alkaline solution. When the solution is acidified the precipitated chromium hydroxide redissolves. Any dichromate present would not interfere *per se*; but in the presence of some remaining unreacted hydrogen peroxide in acid medium it is reduced to chromium^{III} which *in statu nascendi* complexes with EDTA at once. If, however, the solution containing chromium and EDTA is heated at a pH of 2–3, the deep violet chromium^{III} EDTA complex is formed. Any excess EDTA can now be titrated with bismuth solution even at pH values as low as 0·5–0·7. This titration gives chromium alone since the cobalt is present in the bivalent state and is readily replaced by bismuth. In a second aliquot the sum of cobalt and chromium can be determined if the analogous modification of the procedure is followed, *i.e.*, heating the sample with excess EDTA to hasten the complexation of chromium and then making the cooled solution alkaline and oxidising the cobalt with hydrogen peroxide and proceeding as before. Cobalt is then obtained by difference. Unless the acidification of the solution is performed immediately after the oxidation a small amount of chromium may be converted into chromate. In order to reduce this amount rapidly, the addition of a few crystals of ascorbic acid is recommended after the acidification.

Thorium forms a highly stable EDTA complex and hence will be co-titrated. However, the addition of sulphate lowers the apparent stability constant sufficiently to prevent interference. If this masking procedure is applied, the final titration has to be performed at pH about 0·5 in order to avoid the formation of a turbidity on the addition of the bismuth solution.

All metals with a high stability constant for the EDTA complex will be co-titrated, *e.g.*, bismuth, zirconium, indium and gallium (see reference 4) Mercury causes

peculiar time effects and silver is precipitated as oxide at the high pH; it has in addition a catalysing effect on the oxidation of EDTA by hydrogen peroxide, and also speeds the decomposition of the latter. Sometimes a rather violent reaction occurs. Thus both elements should be separated before the cobalt determination.

Iron was already noted in a previous paper[4] as a source of interference. Theoretically it should be co-titrated, as deduced from the high stability of its EDTA complex. In addition, it attacks the indicator and renders the titration impossible. Iron must therefore be absent.

Anions interfere if they exhibit complexing properties, *e.g.*, iodide, citrate, tartrate and fluoride. Chloride, even at pH 0·5 causes a turbidity with bismuth when present in more than trace amounts. Molybdate interferes by blocking the indicator. Tungstate, however, has no influence on the determination.

CONCLUSIONS

As can be seen from some representative results presented in Table I, the accuracy and precision of the method are satisfactory. It is unfortunate that no method could be found to exclude the interference of iron, because it is so frequently allied with cobalt. A previous separation helps but increases the time element in any analysis. The method will, however, give quick and reliable results in the presence of various other metal ions, especially in the presence of nickel and copper.

TABLE I. DETERMINATION OF COBALT IN PURE SOLUTIONS AND IN PRESENCE OF THE FOREIGN METALS

0·1*M* solution of foreign metal added, *ml*	Titration at pH	0·1000*M* EDTA, *ml*		
		Calculated	Required	Difference
None	0·6	4·49	4·47	+0·02
None	1·0	9·25	9·21	−0·04
None	1·0	18·42	18·50	+0·08
None	1·5	23·40	23·56	+0·16
Th, 5 (20 of ml 0·1 M Na_2SO_4 for masking)	0·6	5·20	5·24	+0·04
Mn, 5	0·6	4·60	4·63	+0·03
UO_2^{2+}, 5	0·7	5·63	5·66	+0·03
WO_4^{-2}, 2	0·6	5·67	5·60	−0·07
Ni, 5	0·6	4·58	4·59	+0·01
Ni, 15	0·6	8·56	8·57	+0·01
Ca, 5; Mg, 5	0·6	4·26	4·26	±0·00
Cu, 15	1·5	5·79	5·78	−0·01
Cu, 5; Ni 10	0·6	7·10	7·08	−0·02
Al, 20	0·6	5·32	5·34	+0·02
Ni, 9; Zn, 5; Pb, 8; Cu, 5; Mg, 5	0·6	8·89	8·90	+0·01

The possibility of determining both cobalt and nickel in the same sample by combining the new approach with the method published previously[5] is of special interest. The sample is treated according to the procedure described in the present paper but cooled to 0° by adding ice. Then the back-titration is performed with bismuth, thus giving the sum Ni + Co. The temperature is then raised to room temperature and nickel is replaced by addition of bismuth, the excess of which is

titrated with EDTA, thus giving the value for cobalt. The disadvantage of this procedure is that water condenses from the surrounding air on the cell containing the cooled solution. It is necessary to position the cell free, between the lamp housing and the photo-receptor compartment (see reference 7), and to wipe it dry when the end-point region of the titration curve is recorded. Silicone treatment and operating in a dehumidified room help greatly.

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Zusammenfassung—Eine Methode zur gut selektiven Bestimmung von Cobalt wird beschrieben. Cobalt wird mittels Wasserstoffperoxyd in alkalischem Medium zum Cobalt(III) ÄDTE-komplex oxydiert. Nach Ansäuern wird der Überschuss von ÄDTE mit Wismutlösung photometrisch zurücktitriert unter Verwendung von Brenzkatechinviolett als Indicator. Alkalimetalle, alkalische Erden, Cu, Ni, Zn, Cd, Pb, U, Al und W stören nicht. Bi, Zr, In, Ga und andere Metallionen, die sehr stabile ÄDTE-komplexe formen, werden mittitriert. Mo, Fe, Ag und Hg stören und müssen vorher abgetrennt werden. Die Störung von Mangan wird durch Zusatz von Ascorbinsäure behoben, während Th mit Sulfat maskiert werden kann. Cr(III) wird mittitriert. Durch Anwendung eines Differenzverfahrens und operieren mit zwei aliqueoten Lösungsteilen lassen sich aber sowohl Cr als auch Co bestimmen. Komplexbildende Anionen wie Jodid, Citrat, Tartrat oder Fluorid stören. Gleichfalls stört Chlorid (wenn mehr als in Spuren anwesend) durch Bildung einer Trübung mit Wismut.

Résumé—Le cobalt peut être dosé avec une bonne sélectivité en le transformant à l'aide d'eau oxygénée en milieu alcalin en complexe cobalt(III)-EDTA; l'excès d'EDTA est dosé en retour, par photométrie, en milieu acide par une solution de bismuth avec le violet de pyrocatéchol comme indicateur Aucune interférence n'a été observée avec les alcalins, les alcalino-terreux, Ni, Cu, Cd, Zn, Pb, Al,. U et W. Bi, Zr, In, Ga et les autres métaux formant des complexes très stables avec l'EDTA sont titrés en même temps. Mo, Fe, Ag et Hg gênent et doivent être séparés. L'interférence de Mn peut être éliminée par addition d'acide ascorbique. Th peut être masqué par du sulfate. Cr(III) est titré avec le cobalt, mais en appliquant une méthode différente effectuée avec deux parties aliquotes, Cr et Co peuvent être dosés tous les deux. Les anions complexants gênent, de même que le chlorure qui produit un trouble avec le bismuth.

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ANALYSIS OF GASES AND VAPOURS BY SPECTROSCOPIC TECHNIQUES—I

EMISSION SPECTROSCOPY

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Summary—Theoretical and experimental aspects of the analysis of gases and vapours by emission spectroscopy are discussed and the current literature on molecular emission spectroscopy is reviewed.

At the present time a great deal of information is available on the electronic molecular spectra of a large number of gases and vapours, but surprisingly few applications of such spectra to analytical problems have been described in the literature.

The analysis of mixtures of inert and/or permanent gases is often not easy to achieve using techniques in which the constituents are individually isolated and identified. Of the methods available which do not require preliminary separation of the components of a mixture, those employing a spectroscopic technique are intuitively very attractive, since the manner in which any particular gas or vapour interacts with electromagnetic radiation is characteristic of that substance. The frequency of radiation used can vary from radio frequencies to the extreme ultraviolet. So far, almost all of the published work relates either to the infrared or to the visible and ultraviolet, and most effort has been applied to the study of absorption spectra of substances in the liquid phase.

The aim of this series of papers is to review the available data that have accumulated on the emission and absorption spectra of gases and vapours and to discuss the possible analytical applications of these data. For convenience, the study has been divided into three parts. The first part deals specifically with emission spectroscopy; the second part reviews the absorption of ultraviolet and visible radiations by gases; in the third part of the series some experiments on the analytical application of vapour absorption spectra are described.

EMISSION AND ABSORPTION SPECTROSCOPY

Spectroscopic transitions giving rise to emission and absorption of radiation in the visible or ultraviolet involve a change from one electronic energy level to another. This is the fundamental difference between electronic spectra and infrared spectra, which arise from changes in vibrational and rotational energy only. For a molecule, the electronic transition is necessarily accompanied by simultaneous changes in vibrational and rotational energy, giving rise to band spectra, as distinct from the line spectra given by atoms.

Spectra can be classified into two broad categories, (*a*) emission spectra and (*b*) absorption spectra. Molecular emission spectra arise because some of the molecules

of the system have been excited by physical or chemical means to an electronic level above the ground state. When these molecules revert to the ground electronic state, the excitation energy is given out as electromagnetic radiation. The relationship between initial and final energies (E_1 and E_2) and the frequency of radiation emitted (ν) is the well known one

$$E_1 - E_2 = h\nu \tag{1}$$

where h is Planck's constant.

Molecular absorption spectra arise from the converse process. When a beam of electromagnetic radiation is allowed to pass through a material, some of the frequencies in the beam are removed, *i.e.*, they are absorbed by the material. Those frequencies which are removed again must satisfy the quantal relationship (1), which means that the frequencies absorbed correspond to the energies required to raise the molecules from their ground electronic states to some excited states.

In order to obtain an emission spectrum from any substance it is first necessary to supply energy to the molecules to promote a proportion of them to excited electronic states. This can be done in a variety of physical ways, such as bombardment with high-speed electrons or ions, excitation of a gas in a discharge tube, or the use of an electric arc. Excitation may also be accomplished by chemical means, whereby the excitation energy is supplied as heat given off from an exothermic reaction. This is the case in emission from flames and explosions. The advantages and disadvantages of the various methods of excitation will be discussed later in this paper.

The technique of absorption spectroscopy is, on the whole, simpler than that of emission spectroscopy. In essence one requires only a suitable cell to contain the gas or vapour, having end-windows of quartz for work in the near ultraviolet, or of lithium fluoride for the extreme ultraviolet, together with a source of continuous radiation. The latter is usually a gas discharge lamp using hydrogen or xenon. The spectrograph or spectrophotometer used to detect the absorption is the same as that used in emission work.

Although the emission and absorption of radiation by a gas relates to transitions between the same electronic energy levels, the superficial appearance of the two types, and the regions in which they appear, may be quite different, for reasons given later in this review. For this reason, the proper interpretation of spectra requires a certain amount of experience, which militates against spectroscopic methods as routine analytical procedures.

Both methods are in a way complementary, in the sense that in some cases it is easier to obtain one type, in other cases the other. For instance, molecular oxygen only begins to absorb radiation below 2000 A, which makes it very difficult to obtain a spectrum with instruments readily available in the laboratory, whereas the emission spectrum appears in the region 4000–6000 A, and can readily be obtained using an ordinary quartz spectrograph.

From the analytical standpoint there are two ways in which the electronic spectra can be used, *i.e.*, qualitatively and quantitatively. The qualitative identification of a gas or the components of a gas mixture merely requires that one can positively ascribe a number of bands appearing at certain wavelengths to a particular substance. Because of the complexity of many spectra this often limits the type of mixture that one can analyse with certainty. On the whole, absorption spectra are less complex than emission spectra, and this favours the absorption technique in many cases.

Quantitative analysis requires one to be able to analyse qualitatively as an initial step, and then to be able to relate the intensity of either emission or absorption to the concentration of the gas. The theoretical and practical limitations here are more severe in the case of emission work. For example, the concentration of excited species giving rise to an emission spectrum depends on the means of excitation, the pressure of the gas, and the nature of the other gases present. An absorption spectrum, on the other hand, is usually independent of the nature of other gases present, and depends only on the constancy of the source giving the continuum. As mentioned previously, however, it is not always possible to obtain an absorption spectrum, and it then becomes necessary to use the emission technique even though the difficulties are greater.

THEORY OF EMISSION SPECTROSCOPY

The theoretical interpretation of the emission spectra of diatomic molecules is now well established,[1] and good progress has recently been made in providing a theoretical basis for the interpretation of the spectra of more complex molecules, particularly those which contain one or more aromatic rings.[2]

It is not proposed to attempt any comprehensive treatment of the theory in this review, but to outline some of the more important principles which are essential to the proper application of the technique of emission spectroscopy to gas and vapour analysis.

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Atomic line spectra

The emission spectrum of an atom consists of a series of lines, each of these lines being associated with a transition from one electronic energy level to another. The line spectra of nearly all the elements in the periodic table have been investigated very thoroughly, and are tabulated in various reference books.[3,4] The use of such spectra for analytical purposes has become widespread in the field of metal and alloy analysis, where the sample is volatilised in an arc and the emission spectrum is photographed. This can be followed by plate photometry to give quantitative results of good accuracy. Within the scope of this review, *i.e.*, that of gas and vapour analysis, the only gases giving rise to such line spectra are the inert gases He, Ne, Ar, Kr, Xe and Rn. Spectroscopic analysis for these gases should therefore be amenable to the same type of treatment as that used for metal analysis, apart from the method of excitation used.

In order to utilise the emission spectrum of an inert gas for quantitative analysis it is necessary to relate the intensity of one or more of the atomic lines to the amount of gas present in the system. The methods used to measure spectral intensity, and the difficulties inherent in these measurements, will be outlined in another section. For the moment we shall assume that such intensities can be measured accurately. The intensity of a given line, resulting from a transition between two electronic states, depends on the nature of the initial and final states. If we consider a system of atoms in which a certain proportion of the atoms has been excited from a low energy level, E_1 (say the ground electronic state), to a state of higher energy, E_2, then transitions in which the excited atoms drop to the ground state, emitting radiation, will give rise to a line of frequency ν given by

$$\nu_{1,2} = \frac{E_2 - E_1}{h}. \qquad (2)$$

The rate of emission of this frequency $\nu_{1,2}$ is obviously dependent on the number of atoms involved in the transition per second. If we denote this number by $K_{1\rightarrow 2}$, we can write for the intensity of the line of frequency $\nu_{1,2}$

$$I = A \,.\, K_{1\rightarrow 2} \,.\, h \,.\, \nu_{1,2}, \tag{3}$$

where A is a constant and h is Planck's constant.

$K_{1\rightarrow 2}$ is determined by the time an atom remains in the excited state, called the mean life, which is inversely proportional to the transition probability. We can define the transition probability as the average number of transitions per second of an atom, giving this the symbol $P_{1,2}$ for the transition between states 1 and 2. Then if we have n atoms in the excited state, 2, it follows that

$$K_{1\rightarrow 2} = n \,.\, P_{1,2} \tag{4}$$

Combining equations (3) and (4) we obtain

$$I = A \,.\, n \,.\, P_{1,2} \,.\, h \,.\, \nu_{1,2} \tag{5}$$

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In this equation, A is dependent on the actual experimental conditions, *e.g.*, the type of excitation employed, which can be standardised. $P_{1,2}$ and $h\nu_{1,2}$ will be constant for one particular line. The number of atoms in the excited state, n, will, however, depend on a variety of factors, and in order to put emission spectroscopy on a really quantitative basis these factors must be taken into consideration.

It is obvious that for a given type of excitation, n will depend on the pressure of the gas, since the higher the pressure the more collisions each atom will suffer in unit time. This means that more excited atoms will lose their excitation energy in collision processes, without radiating, than at lower pressures, and hence the intensity of radiation will be less. This phenomenon is easily illustrated practically with a leak tester. At low pressures a gas can be easily made to luminesce, but as the pressure is increased the luminescence progressively decreases until it is totally extinguished. At this point all the excited atoms are being de-activated in radiationless collision processes.

The number n will also depend on the nature of the other gases present. The energy transfer process involved in a collision between an excited atom and a second atom or molecule, resulting in the excited atom losing its energy without radiating, will depend on the nature of this second species. Different molecules vary greatly in the ease with which they can remove electronic excitation from other molecules. If a gas is present which is more efficient at removing the excitation than the gas being excited, then the intensity of emission will be much less than it would be if this gas were absent, at the same total pressure. The converse applies if the foreign gas is less efficient than the parent gas at removing electronic excitation. In this case the emission intensity is greater than for the pure gas.

From the foregoing remarks it is evident that certain restrictions are operative in the use of spectral intensities as a measure of gas concentration. Because of these, any measurement of intensity must be of a comparative nature, since the absolute intensity depends both on the total pressure and on the nature and amount of other gases present.

Molecular band spectra

We shall first consider the emission spectrum of a diatomic molecule. Under low resolution the spectrum appears to consist of a series of bands, instead of the lines which occur in an atomic spectrum. With greater dispersion and higher resolution each of these bands is found to be a group of fairly closely packed lines. This difference between the atomic and molecular spectra results from the fact that whereas an atom has only one means of taking up energy in quantised units, *i.e.*, by changing its electronic configuration, a diatomic molecule has three, the extra two being its vibrational and rotational degrees of freedom. Each electronic transition, which would give rise to one atomic line, therefore gives in the case of a diatomic molecule a series of bands, the gross structure of the band system being determined by the associated changes in vibrational energy, and the fine line structure of each band arising because of simultaneous changes in the rotational energy.

The emission spectrum of a diatomic molecule can be used in the same way as an atomic spectrum for the qualitative identification of gases, by measurement and comparison with the existing data on gases. For this purpose the measurements usually made, and reported in the literature, refer to the so called band heads. Nearly all the bands in the spectra of diatomic molecules have the appearance of being sharp at one end and gradually fading away at the other end. The direction in which the band fades away to longer or shorter wavelengths is termed the direction of degradation. We therefore speak of bands being degraded to longer wavelengths (to the red), or to shorter wavelengths (to the violet). For purposes of qualitative identification it is therefore usually sufficient to measure the wavelengths of as many band heads as possible of the unknown spectrum, and to find which emitter gives bands corresponding to these, with the same direction of degradation.

The use of the emission spectrum of a diatomic molecule for quantitative analytical purposes involves considerably greater theoretical difficulties. Strictly speaking, one would require spectroscopic equipment capable of giving sufficient dispersion and resolution to isolate several of the rotational lines of a band, free from overlap with other lines. Designating the intensity of a single rotational line of frequency ν as I, the following relationship can be derived:

$$I = A \,.\, P \,.\, \nu^4 \,.\, \exp\left(-E_{\text{rot.}}/kT\right) \tag{6}$$

where A is a constant dependent on the total intensity which will depend on the method of excitation and experimental set-up, P is the transition probability, $E_{\text{rot.}}$ is the rotational energy, k is the Boltzmann constant and T is the temperature in °K.

The considerations discussed previously in relation to the use of atomic line spectra for quantitative analysis will apply here, notably the effects of total pressure and foreign gases on the number of de-activating collisions, resulting in radiation loss.

In many cases large dispersion and resolving power are not available, and in these circumstances it would seem obvious to use the band head intensity as a measure of concentration. For this practice small dispersion is actually preferable, since it crowds the rotational lines closer together at the head. The main theoretical objection to the use of the band head for this purpose is that the rotational line structure which forms the head is markedly dependent on the temperature of the system. From equation (6) it can be seen that I is proportional to $e^{-E_{\text{rot.}}/kT}$. The temperature T will in turn be dependent on the total pressure, on the nature of any other gas present,

and on the nature of the excitation. For instance, the rotational temperature of a gas in an electric arc will be much higher than for the same gas in a condensed discharge, resulting in a more complex rotational structure.

Band spectra from polyatomic molecules are necessarily more complex than diatomic molecular spectra. Except in a few cases, there is little regularity in the grouping of the bands, and in general the rotational structure cannot be resolved except with instruments of great resolving power such as large grating spectrographs. Although the theory of polyatomic spectra is now fairly well advanced, it is not nearly as complete as could be desired. This does not, however, prevent one from using the available literature on the recorded spectra of gases as a means of qualitative analysis. Since many polyatomic molecules give rise to headless bands or patches of continuous emission, the use of such spectra for quantitative analysis is much more restricted than in the case of diatomic spectra. Another difficulty encountered here, which will be discussed later, is the fact that in many cases polyatomic molecules tend to dissociate under the excitation conditions necessary to obtain an emission spectrum.

EXPERIMENTAL METHODS OF OBTAINING SPECTRA

(*a*) *Methods of excitation*

The various methods of excitation can be divided into four broad groups, which will be considered individually.

(*i*) *High-frequency discharges.* One of the first methods to be employed utilised the Tesla coil.[5] The Tesla coil produces a high-frequency alternating output of about 50 kV, by means of a mechanical vibrator. Under the influence of such an HF alternating field, free electrons in a gas can acquire sufficient energy to excite and ionise gas molecules, and when the field is sufficiently strong the ionisation process becomes cumulative, leading to a breakdown in the insulating properties of the gas and the production of a luminous discharge. At low frequencies the breakdown process is substantially the same as that found in d.c. discharges, except that since the field is alternating the drift current does not transport electrons away from the space between the electrodes. This results in a simplification of the spectra obtained from a Tesla or any other HF discharge, compared with those obtained using d.c. discharges.

In practice the alternating field is usually applied between a central insulated electrode in the gas to be excited, and the outer wall of the container. Since there are no actual metallic conductors in contact with the gas, there are no lines arising from the metal atoms of the electrodes in the spectra obtained. This is an additional attractive feature of the method.

Two other methods of obtaining HF discharges in gases are extensively used in emission spectroscopy. They are known as the ring discharge and the valve oscillator discharge.[6] In the first of these methods a conventional LC circuit, *i.e.*, one containing an inductance and a capacitance, is used in conjunction with a condensed spark to produce damped oscillations. The inductance is actually wound on the glass or quartz vessel used to contain the gas sample. The strength of the discharge can be controlled by varying the size of the spark gap; and by progressively increasing the strength, the spectra emitted can be made to change from the molecular band type to the line spectra of neutral atoms and ionised atoms.

In the valve oscillator discharge a triode valve is used to maintain continuous radio-frequency oscillations in a tuned circuit. A vessel containing gas at low pressure

may be made to emit radiation by application of this RF power to electrodes within the gas or wound on the outside of the vessel.

All of the methods described give essentially the same type of spectrum and they provide a useful method of obtaining emission spectra free from extraneous lines caused by metallic conductors.

(*ii*) *Discharge tubes*.[5,6] If a tube having metallic electrodes at each end is filled with a gas, and connected to a source of d.c., then as the pressure of gas is gradually decreased, there comes a stage when the insulation of the gas breaks down and the tube acts as a conductor of electric current. At this stage the gas in the tube also begins to glow, the brilliance of the glow depending on the voltage and current being employed at any particular gas pressure. Different regions of the glow have been distinguished by various workers in this field, and some are more luminous than others. The brightest parts, and therefore the most useful for spectroscopic purposes, are known as the positive column and the negative glow.

The excitation process in the positive column the collisions of electrons with gas molecules, and the spectra obtained are predominantly caused by uncharged atoms and molecules. The spectra are however more complicated in appearance than those obtained from high-frequency sources for two reasons. One is that the number of excited electronic states reached in the column is much greater than in the case of the HF discharge, resulting in the appearance of more molecular band systems; and the second is that a considerable amount of decomposition of the gas occurs, leading to the appearance of spectra originating in the molecular fragments produced. Reduction of gas pressure and increase of field intensity both result in higher degrees of excitation.

In the negative glow region, excitation is caused by collisions with electrons from the direction of the cathode; and as a result of this the spectra obtained largely originate from positively charged ions. In order to take full advantage of this region a special type of discharge tube must be used, known as a hollow cathode tube. In this, the cathode is a cylinder and the radiation emitted is almost exclusively from the glow inside this cylinder. Spark lines of the metal used for the cathode are found in the spectra from such tubes, and in fact one of their principal uses is for the production of fine atomic lines for the spectroscopic analysis of small amounts of material. For the examination of molecular spectra, the dimensions of the hollow cathode are usually greater than for this latter type of work.

(*iii*) *Electric arc and spark*. These two methods have been extensively employed for the production of line spectra of metals and of solid or liquid materials capable of being contained in an electrode. They can be further classified as open or enclosed; in the first case the arc or spark is used in air and in the second it is enclosed in an atmosphere of some gas other than air. The application of these sources to the emission spectroscopy of gases is not greatly developed. Obviously, for this application, the enclosed arc or spark is the only one to be considered. Apart from the fact that the source operates in a tube filled with some gas, the technique is the same as that used for the open source. Because of the negative potential-current characteristics of an arc after striking, it is necessary to incorporate a ballast resistor to achieve stability of operation. The actual methods used to obtain steady arc or spark sources are described in various text-books and will not be described further here.[5,6]

The enclosed arc or spark may be operated in various gases and at a variety of pressures, from a few mm pressure of Hg up to many atmospheres. As with the other

methods, reduction of the gas pressure favours a greater degree of ionisation. The use of large pressures of gas is sometimes useful in obtaining spectra not otherwise obtainable, such as those of the hydrides of tin and lead.

The great disadvantage of these two techniques, from the standpoint of gas emission spectroscopy, is that the spectra obtained almost always arise from molecules containing the material used in the poles. There are a few cases, however, where this is not so; for instance, if water vapour is present, such arcs or sparks will give the OH band spectrum, and some, particularly the copper arc, will give in air the NO γ bands.

(*iv*) *Flames.* As with the methods described in section (*iii*) the use of flames in analytical spectroscopy has so far been mainly concerned with the production of line spectra for metal analysis. In general, the degree of excitation attained in a flame is not as high as in the other methods previously described. This results in the absence of bands from ionised species. The spectra obtained from flames largely arises from unstable radicals produced in the combustion process. Since most flames used in practice employ oxygen as the supporter of combustion, the band spectrum of OH is a very prominent feature. When hydrocarbons are present there is also strong emission from CH, C_2, CO, CO_2 and CH_2O. This results in a rather complex total spectrum, in which it is difficult to identify the bands of other entities. This difficulty, combined with the fact that there is usually very little emission attributable to stable polyatomic molecules, makes the method of very limited application in gas emission spectroscopy.

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(*b*) *Methods of recording spectra*

Spectra may be recorded either photographically or photoelectrically. The photographic method employs a spectrograph, which may be of the prism or grating type, and records the whole of the desired spectral region in one operation, on a photographic plate or film. The exposure time will depend on the brilliance of the source employed, and the wavelength region which is of interest will determine the preferable type of photographic emulsion. The method has intrinsic value in exploratory work, since one can see at a glance the wavelength regions in which emission is occurring. Quantitative work, however, requires the use of plate or film photometry, in which one must relate the extent of blackening of the photographic emulsion with the concentration of the emitting species. Although the technique of photographic photometry has been extensively used in the past and can achieve good results when rigorous precautions are taken,[6] it is now accepted that it cannot compete in accuracy and ease of execution with modern photoelectric methods. There are many variables to be kept constant in plate or film photometry; for example, the type of emulsion used, the development time, and the processing technique; and this results in the technique being rather cumbersome and subject to errors.

The photoelectric method, entailing the use of a spectrophotometer, which may be of the automatic recording type, is now used widely for quantitative spectrochemical analysis. Such an instrument, instead of giving the whole spectrum in one operation, scans through the wavelength range, the emitted frequencies being allowed to fall in succession on some type of photoelectric detector. The amplified signal from this may be read off from a meter, or may be used to drive a chart recorder, thus giving a direct measure of the intensity of light at each particular wavelength, without any

need for the rather roundabout series of operations required in work using a spectrograph.

The combination of the two techniques offers the most complete and satisfactory method of spectroscopic analysis for gases, the spectrograph being used for initial exploratory work and the spectrophotometer for detailed quantitative analysis.

INVESTIGATIONS AND ANALYTICAL APPLICATIONS OF MOLECULAR EMISSION SPECTRA

(*a*) *Inert and other permanent gases*

As early as 1922, methods were described for determining the quantity of krypton and xenon in gas mixtures by adding argon as an internal standard.[7] The actual spectroscopic determination of argon in argon-nitrogen mixtures was described by Leimpt and Visser,[8] and Frish[9] developed a method for analysing helium-argon mixtures.

The spectroscope was applied by Gunther and Paneth[10] to the micro-analysis of traces of hydrogen and neon in helium. A year earlier, Klauer[11] had given limits of sensitivity for the detection of hydrogen in helium, helium in hydrogen, hydrogen in argon, and argon in hydrogen-gas mixtures. Analytical working curves have been determined for hydrogen, nitrogen, oxygen and carbon monoxide in the presence of excess helium using a small amount of argon as the internal standard.[12]

The spectrographic determination of deuterium present in mixtures with hydrogen, hydrogen sulphide and ammonia has been described by van Tiggelen.[13]

The determination of nitrogen by emission methods has received a great deal of attention. Monfils and Rosen[14] have examined the determination of traces of nitrogen in argon; and Wijnen and van Tiggelen[15] have described the determination of nitrogen and carbon dioxide in mixtures of these gases and in the presence of oxygen. The relative band intensities of the nitrogen molecular ion spectrum were used by Fan[16] to compare the excitation effect of different species of charged particles on a rarefied air sample. A very detailed study of the emission spectrum of air has recently been published.[17] The relative intensities of the spectra from mildly excited discharges in nitrogen, air, nitrous oxide, oxygen and mixtures of these gases have been studied under high resolution as a function of pressure. A study of the emission band spectrum of nitrogen under pressure had previously been reported by Leycuras.[18]

The spectroscopic determination of nitrogen in respiratory gases is an important aspect of aviation medicine, and progress in this field has been reviewed by White, Lovelace and Hirsch.[19] Commercial instruments known as Nitrometers have been developed which measure the intensity of the nitrogen system after excitation in a gas discharge tube at reduced pressure. Many modifications of this technique are described and the practical limitations are discussed. Methods are also described for the determination of oxygen and carbon dioxide in respiratory gases.

A simple method for determining nitrogen in argon has been suggested. The total intensity of the emission in a discharge tube containing the mixture is compared with the intensity of the nitrogen bands, which are isolated by means of a filter.[20] An alternative approach to the measurement of the purity of inert gases is proposed by Riley[21] who uses the colour and appearance of discharges in gaseous mixtures as a criterion of the purity.

Preliminary studies on the excitation of the spectra of inorganic gases by high frequency excitation have been reported[22] from the authors' laboratory, and quantitative applications are at present under investigation.

Data on the emission molecular spectra of many gases including bromine, carbon monoxide, carbon dioxide, chlorine, fluorine, hydrogen, helium, nitrogen, ammonia, nitrous oxide, oxygen, sulphur monoxide and sulphur dioxide are tabulated in the reference work of Pearse and Gaydon.[5]

(*b*) *Benzene and benzene derivatives*

Publications devoted to analytical applications of polyatomic emission molecular spectra are almost non-existent. To date, interest has been concentrated on obtaining molecular spectra characteristic of an undissociated molecule, or, where fragmentation has occurred in the process of excitation, on attempts to identify the fragments. The first major investigation of the emission spectra of organic compounds was made by Stewart and co-workers[23] in the 1920's. Nearly one hundred and forty compounds were excited with a form of Tesla discharge, and the compounds which emitted radiations were grouped into five main categories depending on the general appearance of the resultant spectra. In most cases, continuous bands of emission were obtained because of the low dispersing power of the spectrographic equipment used. Attempts by Austin and Black[24] to use these spectra to identify the purity of a solvent were not successful, but these authors succeeded in confirming the wavelengths of the benzene bands and in identifying the nature of the side products formed in discharges passed through a number of organic vapours. A spectroscopic study of the decomposition and synthesis of organic compounds by electrical discharges was made a couple of years later, and dissociation of the organic molecule into atomic and ionic fragments was found to be an important factor in the maintenance of the discharge.[25]

A continuing series of papers by Schuler and co-workers has done much in recent years towards building up an understanding of the source of the spectra. In 1941, pure emission spectra of undecomposed benzene derivatives were obtained by electron collision in the glow discharge.[26] In the following year, a further series of benzene derivatives were studied by means of a glow discharge in krypton and hydrogen. In the ultraviolet region, the emission corresponded to the absorption spectrum, but in the visible range additional bands were observed which were ascribed to the dissociation of activated phenyl radicals.[27] A later publication demonstrated the similarity of the natural decomposition spectra of benzene derivatives and the spectra resulting from their phospholuminescence in the solid state.[28] Direct proof of the existence of short-lived aromatic radicals, based on their emission spectra, was put forward by Schuler and Reinebeck[29] in 1949, and the spectrum of the CHO radical was found in the emission spectrum of formaldehyde.[30]

In 1950 a new type of discharge tube was designed,[31] and a method of varying the excitation conditions for organic substances was proposed.[32] By examining benzene evaporated into a cell containing helium, four new spectra were found.[33] By increasing the naphthalene vapour pressure in a helium discharge a new spectrum besides the helium line and bands of C_2 and CH appeared.[34] Five types of compounds, including acetylene, ethylene and aromatic molecules, were subsequently studied to find the groups responsible for the newly found spectra.[35] Further work using the mono-derivatives of benzene[36] indicated that the common fragments

observed in the glow discharge could possibly be one of four species. Subsequent work by Walker and Barrow[37] showed that the simplest interpretation involves the presence of an emitter such as C_6H_5C. These bands were found under excitation conditions intermediate between those giving the spectrum of the complete molecule and those which result in appreciable dissociation into small fragments, *e.g.*, CH. A vibrational analysis of the visible spectrum of the benzyl radical has recently been proposed.[38]

In 1954, Schuler and Reinebeck[39] surveyed the results of emission spectroscopy of organic molecules in the low pressure discharge, and concluded that the spectra obtained did not correspond to transformations between highly excited states of the molecules introduced, but indicated instead the fragmentation of these molecules. In subsequent studies, the excitation conditions were varied and it was shown that the spectra obtained were reproducible if the conditions of discharge were standardised.[40,41,42] It was suggested that collision between the excited and non-excited initial molecule plays an important part in the phenomenon of luminescence of organic molecules in a glow discharge. Schuler's results on benzene and chlorobenzene have been confirmed by Danilova,[43] and confirmation of decomposition and synthesis reactions in the glow discharge has been provided by Nishi and Hamanura.[44]

The emission spectra of benzene, toluene and xylene vapours excited by a high frequency (Tesla type) discharge have also been studied by Agirbiceanu and Hagiescu.[45] Solid polymerisation products and continuous emission backgrounds were observed, but none of the spectra suggested the presence of free radicals, fragments or impurities. The benzene spectrum had previously been re-examined by Asundi and Padhye[46] and the same authors had reported a series of emission bands for toluene.[47] The emission bands of aniline produced by a variety of excitation methods had also been recorded.[48] A high frequency electrodeless discharge was used by Robinson[49] to excite the spectra of benzaldehyde and acetophenone. A later, more complete analysis of the benzaldehyde spectrum has been reported by Garg and Singh[50] who excited the flowing vapour with an uncondensed transformer discharge. The same type of discharge was used by Upadhya[51] to study the emission bands of benzotrifluoride.

Asundi and Joshi have used a high-frequency discharge to obtain emission spectra from benzonitrile[52] and *p*-dichlorobenzene.[53] An ozoniser type of discharge was used to produce an emission spectra from the three isomeric fluorotoluenes.[54] Spectra for tetrahydronaphthalene[55] and naphthalene[56] vapours have recently been reported.

Paillous has made an intensive study of the emission spectra of toluene,[57] fluorobenzene,[58] benzonitrile[59] and aniline.[60] Over two hundred bands were identified in each case and a vibrational assignment of the frequencies was attempted.

(*c*) *Miscellaneous organic compounds*

The emission spectrum of formaldehyde was found by Schuler and Reinebeck[30] to be identical with the fluorescence spectrum. The same compound was studied by Robinson[61] using a high dispersion spectrograph and a technique originally developed in a study of the spectrum of acetaldehyde.[62] The rotational structure of the emission bands of formaldehyde has been discussed by Fauris[63] and new bands in the emission spectra of acetaldehyde were reported by Régnier.[64]

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The glow discharge apparatus used previously by Schuler and Reinebeck to study benzene derivatives was also utilised by these workers to study the emission of biacetylene.[65]

The passage of a high-frequency discharge through methane and the vapours of aliphatic alcohols was found to produce the spectra of decomposition fragments.[66] Spectra attributable to decomposition products were also detected in the emission spectra of CCl_4 and $C_2F_2Cl_2$.[67]

The decomposition of compounds under high frequency excitation was utilised by Keller and Smith[68] in the development of a spectrographic method for the detection of halogens. Excellent iodine, bromine and chlorine identifications were obtained with organic and inorganic compounds, and the limits of detection were of the order of a fraction of 1%.

Another analytical application of gaseous discharges has been the development of a Tesla discharge detector for gas chromatography.[69] The discharge of a gas is visibly altered by small amounts of added vapour, and the new detectors measure either the emitted light intensity or the d.c. signal produced by inserting a pair of probe electrodes asymmetrically in the discharge.

DISCUSSION

The general precautions that must be taken to ensure reliable results in the spectrochemical analysis of gases have been listed by Twyman.[70] Twyman, as would be expected from the previous theoretical discussion, has emphasised that the gas pressure in the tube and the conditions of excitation must be carefully controlled, because the ratio of the line intensities of two components may vary with pressure, even though the two gases are present in the same proportion. Twyman also advises that measures be taken to avoid the effects of a variable concentration of a third constituent, since the presence of a third gas can influence the ratio of the line intensities of two components. Because the rate of "clean up" in the electric discharge varies with the nature of the gas, the apparent proportions of the gases in a sample may change with the time of running of the discharge.

It is further suggested that care must be taken to remove occluded gases from the inside walls of the discharge tube and from the electrodes (if inside the tube) before filling with the sample. Achievement of this ideal often requires prolonged baking of the cell at temperatures up to 450°. The importance of the condition of the cell has been emphasised by Frish,[9] who has also reviewed the problems associated with the spectrochemical analysis of gases. One of the main difficulties encountered by Frish was the fact that the composition of the gaseous mixture varied during analysis because of adsorption and desorption on the tube walls. Another important problem was that of establishing the optimum conditions for the excitation of the spectrum of the impurities being analysed, since the composition of the mixture had a strong effect on the conditions of discharge.

These difficulties have not prevented the successful analysis of gases by spectroscopic means; and, in fact, the spectroscopic analysis of respiratory gases now appears to have become the accepted technique.[19] Great care must be paid to the standardisation of conditions, but successful extension to the analysis of the rare gases seems highly feasible and experimental work along these lines is now proceeding in our laboratories.

On the other hand, extension of the emission technique to the analysis of organic compounds seems highly improbable. Tesla excitation is said to cause less decomposition of the excited species than alternate modes of excitation, but a constant flow of vapour is considered advisable.[5] However, decomposition does still occur and at least two attempts[22-24] have been made to analyse the products deposited on the walls of the glass retaining vessels. In both cases the compounds were concluded to be condensed or polymerised molecules. In a spectroscopic study of the chemical reactions which occur in electrical discharges through organic vapours[25] it was found that the simple ionisation of the molecules and the resultant formation of clusters was less important, and the breaking down into molecular and atomic fragments more important than has heretofore been supposed. More recently, Schuler and Stockburger[42] examined the spectra of a number of substituted benzene derivatives, and found that the excitation caused a splitting off of a small molecule, the remainder being stabilised by double-bond formation, ring-closure or dimerisation. In another study[71] a high-frequency discharge through flowing carbon tetrachloride vapour was found to yield the spectrum of CCl, produce free chlorine, and deposit a small carbonaceous residue.

Apart from complications caused by fragmentation and association of organic compounds during excitation, the complexity of the molecular spectrum produced is in most cases too great for use in analysis.

A final detrimental factor is the ready contamination of the spectra by trace impurities such as air, since these impurities are often preferentially excited. For example, the heating of some organic compounds has been found to release enough air from the sample and the walls of the cell to produce an intense spectrum of nitrogen on excitation.[71] The same detrimental effect was obtained in evacuated cells containing low pressures of gases such as hydrogen, carbon dioxide, chlorine, methane, *etc.*, possibly because of slight leaks of air into the cell.

All forms of emission spectroscopy are renowned for their sensitivity and the characteristic nature of the spectra produced, and these probably constitute the greatest advantages of the technique. In the gaseous phase, if a species is readily excited and gives either a line or simple band spectra, *e.g.*, argon, nitrogen, oxides of carbon, *etc.*, then careful control of conditions permits the development of satisfactory analytical methods. On the other hand if a species is not readily excited, or if the resultant spectrum is fairly complex, emission techniques are far less satisfactory than most other alternate techniques that may be applied to the same problem. Analysis based on the absorption spectrum of a molecule could be a desirable alternative, since there is less tendency for fragmentation or association of excited species; the spectrum is usually comparatively simple; and the interference of impurities on cell walls, *etc.*, is virtually unknown. However, the application of electronic absorption spectra to problems involving the gaseous phase does not appear to have received much attention. The possibilities of this approach will be reviewed in Part II of this series.

Acknowledgment—One of us (W. F. P.) wishes to acknowledge with thanks the grant of study leave from the University of New South Wales, Australia, and the Research Fellowship from the Queen's University, which have made participation in this project possible.

Zusammenfassung—Theoretische und experimentelle Belange der Analyse von Gasen und Dämpfen mittels Emissionsspektroskopie werden diskutiert. Eine Übersicht über die derzeitige Literatur über Molekularemissions-spektroskopie wird gegeben.

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Résumé—Les auteurs ont examiné les aspects théoriques et expérimentaux de l'analyse des gaz et des vapeurs par spectroscopie d'émission et ont passé en revue la littérature courante sur la spectroscopie d'émission moléculaire.

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SHORT COMMUNICATION

The use of vanadium^{V}-sulphosalicylic acid complex as a redox indicator

(*Received* 6 *June* 1961: *Accepted* 15 *July* 1961)

In a previous communication[1] it was reported that vanadium^{V} gives an intense turquoise-blue colour with sulphosalicylic acid in concentrated sulphuric acid and that the colour reaction is specific and very sensitive for the detection of vanadium^{V}. During our studies on the nature of the complex, it was found that vanadium^{IV} gives a negative colour test and that the blue colour developed by the reagent with vanadium^{V} is discharged on the addition of a reducing agent like iron^{II}, uranium^{IV} or hydroquinone. It was also observed that the blue colour is restored by the addition of cerium^{IV} solution. This reversible property of the complex has been further investigated to see if the complex can be used as a redox indicator.

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EXPERIMENTAL

Our experiments have shown that

(a) sulphosalicylic acid undergoes oxidation by potassium permanganate or cerium^{IV} sulphate in a sulphuric acid medium, but phosphoric acid prevents the oxidation of sulphosalicylic acid by cerium^{IV} sulphate although not by potassium permanganate,

(b) there is no appreciable reaction between sulphosalicylic acid and potassium dichromate within the time required for a titration,

and (c) the complex dissociates at higher temperatures.

In view of these observations, it may be concluded that a small amount of vanadium^{V}—sulphosalicylic acid complex may be used as an internal indicator in the titration of iron^{II} with potassium dichromate in 20*N* sulphuric acid (an acidity required to give a sufficiently intense blue colour when vanadium^{V} and sulphosalicylic acid are mixed) and with cerium^{IV} sulphate in 20*N* sulphuric acid in the presence of phosphoric acid. It is also evident that it cannot be used as an indicator for titrations with potassium permanganate because it discharges the colour of the complex by oxidising the sulphosalicylic acid ligand.

Indicator solution

This is prepared by dissolving 0·12 g of ammonium vanadate and 2 g of sulphosalicylic acid in 100 ml of concentrated sulphuric acid. A volume of 0·2 ml of this solution is found to be sufficient for 50 ml of titration mixture. It is not necessary to prepare this solution beforehand, because the complex can be produced *in situ* by adding the requisite quantities of ammonium vanadate and sulphosalicylic acid solutions separately to the titration mixture.

Recommended titration procedure

An aliquot of iron^{II} sulphate solution is taken and sufficient water and concentrated sulphuric acid are added to make up the volume to 50 ml and to keep the acidity at 20*N* at the end of the titration. The solution is cooled to room temperature and 0·2 ml of the indicator solution is added. This solution is titrated, cooling it whenever necessary, with potassium dichromate or with cerium^{IV} sulphate solution after adding 5 ml of 80% phosphoric acid. The end-point is indicated by the solution changing its colour to greenish-blue on the addition of an excess drop of the oxidant. In titrations with potassium dichromate the titration mixture, if necessary, can be diluted with 20*N* sulphuric acid to prevent the green chromium^{III} sulphate interfering with the detection of the end-point. The titres are found to agree with the values obtained from potentiometric titrations carried out at the same acidity.

Redox potential of indicator

The transition potential of the vanadium^{V}–sulphosalicylic acid complex as an indicator in the titration of iron^{II} sulphate solution with cerium^{IV} sulphate solution in 20*N* sulphuric acid was determined according to the procedure of Belcher, Nutten and Stephen,[2] and found to be 950 ± 5 mV (N.H.E.).

Acknowledgement—The authors wish to thank Professor G. Gopala Rao for his interest in the work.

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Summary—In a previous communication it was reported that vanadium^{V} gives an intense turquoise-blue colour with sulphosalicylic acid in concentrated sulphuric acid and that the colour reaction is specific and very sensitive for the detection of vanadium^{V}. During our studies on the nature of the complex, it was found that vanadium^{IV} gives a negative colour test and that the blue colour developed by the reagent with vanadium^{V} is discharged on the addition of a reducing agent like iron^{II}, uranium^{IV} or hydroquinone. It was also observed that the blue colour is restored by the addition of cerium^{IV} solution. This reversible property of the complex has been further investigated to see if the complex can be used as a redox indicator.

Zusammenfassung—In einer früheren Mitteilung wurde über einen tiefblauen Komplex von Vanadin(V) mit Sulfosalizylsäure in koncentrierter Schwefelsäure berichtet. Die Färbung ist spezifish für Vanadin(V) und die Reaktion ist sehr empfindlich. Während weiterer Untersuchungen wurde gefunden, dass Vanadin(IV) diese Reaktion nicht gibt. Die Färbung des Vanadin(V) komplexes wird durch Reduktionsmittel wie Eisen(II), Uran(IV) oder Hydrochinon ausgebleicht, erscheint jedoch auf Zusatz von Cer(IV) wieder. Die Reversibilität der Reaktion wurde untersucht um zu sehen, ob der Komplex als Redoxindicator Verwendung finden kann.

Résumé—Dans une communication précédente, nous avons indiqué que la vanadium(V) donne une coloration bleu turquoise intense avec l'acide sulfosalicylique dans l'acide sulfurique concentré et que cette réaction colorée est spécifique et très sensible pour déceler le vanadium(V). Pendant notre étude sur la nature du complexe, nous avons trouvé que le vanadium(IV) ne donne pas cette réaction et que la couleur bleue obtenue avec le vanadium(V) est déchargée par addition d'un agent réducteur comme le fer(II), l'uranium(IV) ou l'hydroquinone. Nous avons alors observé que la couleur bleue réapparaît par addition d'une solution de cérium(IV). Cette propriété réversible du complexe a été étudiée ultérieurement pour voir si le complexe peut être utilisé comme indicateur rédox.

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NOTICES

Material for this section should be sent directly to the Assistant Editor

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ARGENTINA

Sunday–Saturday 16–22 *September* 1962: **Eighth Latin-American Congress of Chemistry,** on the occasion of the *Fiftieth Anniversary of Asociación Química Argentina.* Buenos Aires.

The congress is open to chemists from all countries and will be divided into the following sections:

1. Inorganic and Radio-Chemistry
2. Physical Chemistry
3. Organic Chemistry
4. Biological Chemistry
5. Analytical Chemistry
6. Food Chemistry
7. (a) Pharmaceutical Chemistry
   (b) Pharmaceutical Industries
8. (a) Industrial Chemistry
   (b) Chemical Engineering
9. History of Chemistry and Chemical Education.

Further information can be obtained from the Secretary, Octavo Congreso Latinamericano de Quimica, Casilla de Correo 2153, Buenos Aires, Argentina.

CANADA

Sunday–Friday 19–24 *August* 1962: **VIII International Congress for Microbiology:** *Canadian Society of Microbiologists* and *Canadian Committee on Culture Collections of Micro-organisms* under the auspices of the *International Association of Microbiological Societies.* Queen Elizabeth Hotel, Montreal.

Three symposia or panel discussions will be held each morning and formal invitations have been issued to the speakers. Concurrent paper-reading sessions will normally be held each afternoon.

The following programme has been arranged for the panel discussion on **Automation and Control of Process Variables in Industrial Microbiology:**

J. J. H. HASTINGS (London, England) — *Application of Automation to Processes, Analysis, Assay, and Computation.*

H. M. SHER (London, England) — *Measurement and Control of Physical Variables.*

Discussant—H. J. HROCH

J. F. PAGANO (New Brunswick, U.S.A.) — *Automatic Devices for Microbiological Assay of Antibiotics.*

Discussant—J. M. KELLY

V. L. SINGLETON (Davis, U.S.A.) — *Applications of Liquid Chromatographic Techniques to the Production and Analysis of High Quality Products.*

Discussant—J. R. GERKE

A. FERRARI (Chauncey, U.S.A.) — *Application of Methodology of Chemical and Biochemical Analysis with an Autoanalyzer Instrumental System.*

Discussants—G. E. REINHARDT, G. E. SCHAIBERGER

J. A. KEARNS (New York, U.S.A.) — *The Electronic Computor in Microbiological. Control.*

Discussant—G. E. BOND

Further information can be obtained from the Secretariat, VIII International Congress for Microbiology, 3574 University Street Montreal, Canada.

FRANCE

La 5ème réunion de la Commission Internationale d'Analyses (CIA) du **Comite International de la Detergence** (CID) s'est déroulée à Paris, les Lundi 9 et Mardi 10 Octobre 1961, sous le présidence du Professeur JACINI (Italie).

Huit pays participaient à cette réunion: Allemagne, Belgique, Espagne, France, Grèce, Italie, Pays-Bas, Suisse. On remarkuait aussi la présence d'un délégué de *l'Association Internationale de la Savonnerie et de la Detergence* (AIS), qui est membre consultatif du CID, et d'un observateur de *l'Organisation Internationale de Normalisation* (ISO).

Au cours de l'année 1960/1961, différentes analyses circulaires ont été effectuées dans les pays membres de CIA en suivant les méthodes d'analyses en examen au sein de cette Commission et en utilisant des produits définis fournis par des laboratoires désignés a cette fin. Les résultats de ces analyses se sont révélés concordants. Après discussion des résultats obtenus et certaines modifications suggérées en séance, les méthodes d'analyses des *alkylsulfonates de sodium* et *alkylsulfates primaires de sodium* pourrant bientôt être considérées comme suffisamment précises pour être soumises à l'ISO aux fins d'homologation internationale. Auparavant, ces méthodes seront comparées au sein des Commissions nationales avec celles qui seront basées sur l'emploi des résines échangeuses d'ions.

Deux autres méthodes, moins avancées, seront étudiées par analyses-circulaires en 1961/1962; la séparation des alkylsulfates d'une part, et des alkylsulfonates de l'autre, des *non-ionique*. En ce qui concerne ces derniers produits, il a été jugé bon de réunir prochainement certains membres de CIA à Bruxelles, pour une "journée d'information non-ionique".

Quant aux *savons purs*, les méthodes d'analyses adoptees sont celles de *l'Union Internationale de Chemie Pure et Appliquee* (IUPAC). Par ailleurs, et en accord avec cet organisme, quatre méthodes supplementaires figurent au programme de travail de CIA dont deux (dosage du glycérol, détermination de l'insaponifié) seront bientôt circulairisées aux membres de la Commission.

Il a été ensuite décidé que la prochaine session de la CIA se tiendrait à Bruxelles, sur invitation du Comité Belge de la Detérgence, en Septembre, 1962. Le délégué grec a par ailleurs invité ses collègues à se reunir à Athenes en 1963.

POLAND

Among the 225 participants at the **Third Polish Spectral Emmission Conference** in September, 1961 (see also *Talanta*, 1961, **8**, 174), there were 63 from Hungary, 21 from German Democratic Republic, 10 from Czechoslovakia, 3 from France, and 1 each from Russia, Italy, Yugoslavia and Bulgaria.

In the scientific programme 54 short communications were announced, covering all fields of emission spectroanalysis. The majority of the communications dealt with the analysis of non-conductive samples (18), the analysis of solutions (14) and general problems (13). The Organisation Committee invited 6 scientists to deliver plenary lectures on the most important topics in emission spectroscopy: Dr J. ŚWIETOSLAWSKA (Poland), The Addition Method in Emission Spectral Analysis; Dr. T. TÖRÖK (Hungary), Actual Possibilities and Problems of the Quantitative Evaluation of Spectra on Photographic Plates; Dr. H. MORITZ (German Democratic Republic), The World Development of Spectral Analysis; Ing. M. MATHERNY (Czechoslovakia), The Emission Spectrochemistry of Solutions; Professor A. K. RUSANOV (Russia), Particular Features of the Spectral Analysis of Powder Materials; Dr. J. CZAKOW (Poland), The Quantitative Spectral Analysis of Traces.

UNITED KINGDOM

Wednesday 10 *January* 1962: Symposium on **Developments in Gas Chromatography as Applied to Polymers:** Mr. D. H. DESTY, Dr. C. A. FINCH and Dr. R. S. LEHRLE: *Society for Analytical Chemistry, Midlands Section*. The University, Edgbaston, Birmingham, 15. 2.30 p.m.

Wednesday 10 *January* 1962: **Precision Balances—History, Development and Techniques:** Mr. A. O. BROOKS: *Aberdeen and North of Scotland Sections* of *Chemical Society, Royal Institute of Chemistry* and *Society for Chemical Industry*. Chemistry Department, University, Old Aberdeen.

Friday 12 *January* 1962: **Annual General Meeting** followed by **Radioactivity Measurements in Monmouthshire:** Dr. G. V. JAMES: *Society for Analytical Chemistry, Western Section*. University College, Cardiff.

Tuesday 16 *January* 1962: **Some Aspects of the Work of a Public Analyst:** Mr. R. W. SUTTON: *Royal Institute of Chemistry, East Midlands Section*. Derby and District College of Technology, Kedleston Road, Derby. 7.30 p.m.

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Wednesday 17 *January* 1962: **Complexometric Titrations:** Professor H. M. N. H. IRVING: *Royal Institute of Chemistry, North Wales Section.* Flintshire Technical College, Connah's Quay, Nr. Chester.

Wednesday 24 *January* 1962: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Friday 26 *January* 1962: **Annual General Meeting** followed by **Application of Analysis to Research Problems in the Gas Industry:** Mr. G. R. BOREHAM: *Society for Analytical Chemistry, Scottish Section.* Grosvenor Restaurant, Gordon Street, Glasgow. 1.30 p.m.

Saturday 27 *January* 1962: **Annual General Meeting** followed by **The Work of the Laboratory of the Government Chemist:** Dr. D. T. LEWIS: *Society for Analytical Chemistry, North of England Section.* City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Monday–Friday 9–13 *April* 1962: **Feigl Anniversary Symposium:** *Society for Analytical Chemistry, Midlands Section,* under the patronage of *I.U.P.A.C.* University, Edgbaston, Birmingham, 15 (see also *Talanta*, 1961, **8,** 561 and 765).

Plenary lectures will be given by:

Professor Dr. Ing. F. FEIGL (Ministry of Agriculture, Rio de Janeiro, Brazil)	*The Development of Spot Test Analysis and the Chemistry of Specific, Selective and Sensitive Reactions.*
Professor R. BELCHER (University of Birmingham, U.K.) and Professor P. W. WEST (Louisiana State University, U.S.A.)	*An Appreciation of the Contribution of Fritz Feigl to the Development of Analytical Chemistry.*
Professor F. WELCHER (University of Indiana, U.S.A.)	*The Development of Organic Reagents for Inorganic Analysis.*
Professor H. MALISSA (Technical University, Vienna, Austria)	*From Spot-Tests to Spot-Colorimetry.*

The detailed scientific programme, subject to additions and minor alterations, is as follows:

D. M. W. ANDERSON (University of Edinburgh, U.K.)	*Analytical Applications of Infrared Spectroscopy.*
C. V. BANKS (Iowa State University, U.S.A.)	*Vicinal Dioximes as Analytical Reagents.*
E. BERG (Louisiana State University, U.S.A.)	*Separation of Some Transition Metals by Counter-Current Extraction.*
J. BERGER (Danish School of Pharmacy, Denmark)	*Derivatives suitable for Identification of Organic Acids.*
E. BISHOP (University of Exeter, U.K.)	*Differential Electrolytic Potentiometry.*
T. BURKHALTER (Texas Instruments Inc., U.S.A.)	*Chromatographic Determination of Trace Elements in Capacitor Grade Tantalum.*
J. K. CARLTON (Louisiana State University, U.S.A.)	*Streak Reagents for Colourless Zones in Adsorption Chromatography.*
R. A. CHALMERS (University of Aberdeen, U.K.)	*Redox Potentials and Qualitative Analysis.*
F. CLANET (C.E.A., Radiochemical Laboratory, France).	*Spot-Testing for Transuranic Elements.*
D. COOKE (Cornell University, U.S.A.)	*Atomic Absorption Spectroscopy with Continuous Sources.*
T. A. DAVIES [International Nickel Co. (Mond) Ltd., Birmingham, U.K.]	*Application of Solids Mass Spectroscopy to Metallurgical Analysis.*
C. DUVAL (C.N.R.S. Research Laboratory, France)	*The Existence of the Uranyl Ion.*
G. V. M. DUYCKAERTS (University of Liege, Belgium)	*Extraction of Phosphate Esters.*
P. J. ELVING (University of Michigan, U.S.A.)	*Microanalysis with the Graphite Indicating Electrode.*
W. T. ELWELL (I.C.I. Ltd., Metals Division, Birmingham, U.K.)	*Atomic Absorption Spectroscopy.*

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L. Erdey (Technical University, Budapest, Hungary)	*Standard Sulphur Solutions for the Non-Aqueous Titration of Cyanide and Selenium.*
H. Freiser (University of Arizona, U.S.A.)	*Use of Organic Reagents in Solvent Extraction.*
D. Gibbons (A.E.R.E., Harwell,U.K.)	*Computer Coupled Automatic Activation Analysis.*
D. Goldstein (Ministry of Agriculture and Mineral Products, Brazil)	*A New Spot-Test for Sulphur in Organic and Inorganic Compounds.*
L. Gordon (Case Institute of Technology, U.S.A.)	*Precipitation Processes.*
J. B. Headridge (University of Sheffield, U.K.)	*Analytical Application of Redox Reactions in Hydrofluoric Acid.*
H. M. N. H. Irving (University of Leeds, U.K.)	(to be announced)
W. Kemula (University of Warsaw, Poland)	*Chromato-polarography.*
I. M. Kolthoff (University of Minnesota, U.S.A.)	*Induced Reactions.*
G. Kortum (University of Tubinger, Germany)	*Diffuse Reflectance Spectroscopy in Analytical Chemistry.*
H. A. Laitinen (University of Illinois, U.S.A.)	*Molybdenum Catalysed Reduction of Perchlorate.*
D. T. Lewis (Laboratory of the Government Chemist, London, U.K.)	*The Use of Bismuth Radionuclides in Analysis.*
R. J. Magee (Queen's University, Belfast, U.K.)	*Spectrophotometric Determination of Niobium in presence of Tantalum and Associated Elements.*
G. Mattock (Electronic Instruments Ltd., Richmond, U.K.)	*The Analytical Applications of Alkali Cation-Sensitive Electrodes.*
A. C. Menzies (Hilger & Watts Ltd., U.K.)	*Aspects of Atomic Absorption Spectroscopy.*
G. W. C. Milner (A.E.R.E., Harwell, U.K.)	*Electrochemical Analysis in Atomic Energy.*
F. L. Moore (Oak Ridge National Laboratory, U.S.A.)	*High Molecular Weight Amines—Versatile Extractants.*
G. H. Morrison (Cornell University, U.S.A.)	*Extension of Sensitivity in Trace Element Analysis.*
L. J. Ottendorfer (Technical University, Vienna, Austria)	*Chronoautoradiographic Estimation of Small Amounts of Radioactive Materials.*
F. H. Pollard (University of Bristol, U.K.)	*New Reagents Specially designed for Chromatographic Use.*
R. Přibil (Academy of Sciences, Prague, Czechoslovakia)	*New Rapid Methods for Alloy Analysis.*
R. C. Rooney (Southern Analytical Ltd., Camberley, U.K.)	*Recent Developments in Cathode Ray Polarography.*
E. Sawicki (Health Dept., Cincinnati, U.S.A.)	*Spot-Test Detection and Spectrophotometric Determination of Formic Acid.*
P. Senise (University of Sao Paulo, Brazil)	*Aspects of Extractability of Phosphonium Salts and Related Compounds.*
E. Schulek (L. Eötvös University, Budapest, Hungary)	*Determination of Small Amounts of Carbon Dioxide from Decarboxylation of Organic Compounds.*
A. A. Smales (A.E.R.E., Harwell, U.K.)	*Recent Analytical Work using Specific and Sensitive Nuclear Methods.*
G. F. Smith (University of Illinois, U.S.A.)	*Deuterium Perchlorate.*
H. Specker (Dortmund Institute of Spectroscopy, Germany)	*Trace Analysis by "Inverse Polarography".*
W. I. Stephen (University of Birmingham, U.K.)	*Reagents for the Nitrate Ion.*
H. Suter (Celanese Chemical Co., Clarkwood, Texas, U.S.A.)	(to be arranged)
S. Viebel (Polytechnic Institute, Copenhagen, Denmark)	*Detection, Characterisation and Estimation of Carboxylic Acids and Esters.*

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A. WALSH (C.S.I.R.O., Melbourne, Australia)	*Atomic Absorption Spectroscopy in Australia.*
H. F. WALTON (University of Colorado, U.S.A.)	*New Ion-Exchange Methods for Analytical Separation.*
H. WEISZ (University of Freiburg-Breisgau, Germany)	*Semi-quantitative Analysis by Spot Reactions: A Review of New Reactions.*
P. W. WEST (Louisiana State University, U.S.A.)	(to be announced)
A. F. WILLIAMS (I.C.I. Ltd., Nobel, Division, Stevenston, U.K.)	*Quantitative Aspects of Gas Chromatography and the Analysis of Blasting Explosives.*
C. L. WILSON (Queen's University, Belfast, U.K.)	*Separation and Identification of Some Anions on the Microgram Scale.*
H. N. WILSON (I.C.I. Ltd., Billingham Division, U.K.)	*X-ray Fluorescence.*
P. ZUMAN (C.S.A.V. Polarography Institute, Prague, Czechoslovakia)	*Polarography in Functional Analysis.*
J. ZYKA (Charles University, Prague, Czechoslovakia)	*New Oxidation-Reduction Titrations.*

Sunday–Saturday 9–15 *September* 1962: **Fifth Triennial Summer School in Analytical Chemistry:** *Royal Institute of Chemistry* with the participation of *Society for Analytical Chemistry*. Manchester College of Science and Technology.

The School will consist of four separate, but concurrent, courses:

Course I—*Physical Methods of Organic Chemistry*

Course Leader: Dr. D. W. MATHIESON, Reader in Pharmaceutical Chemistry, School of Pharmacy, London, W.C.1.

Course II—*Recent Developments in Inorganic Analysis*

Course Leader: Mr. W. T. ELWELL, Chief Analyst, I.C.I. Ltd., Metals Division, Witton, Birmingham, 6.

Course III—*Determination of Toxic Substances in the Air and Effluents*

Course Leader: Mr. H. E. STAGG, Chief Analyst, I.C.I. Ltd., Dyestuffs Division, Blackley Manchester.

Course IV—*Newer Instrumental Techniques*

Course Leader: Dr. V. S. GRIFFITHS, Reader in Spectroscopy, Battersea College of Technology, London.

Further information may be obtained from Mr. D. G. CHISMAN, Education Officer, Royal Institute of Chemistry, 30, Russell Square, London, W.C.1.

The Fourth Edition (1961) of the **Directory of Independent Consultants,** compiled by the Royal Institute of Chemistry, is now available and can be supplied gratis to bona fide enquirers for consulting services in chemistry and related subjects. It covers a wide range of consultant services offered by 156 independent practices in Great Britain and Ireland, operated and controlled by Fellows or Associates of the Royal Institute of Chemistry, which are not part of any other organisation.

The general plan of the directory is similar to that adopted in other editions, but the basis of the subject guide has been revised to take account of the number and variety of fields of specialisation, and to make it easier to refer to the main section of the directory in finding consultants most likely to help in a particular field.

Further lists of books received from U.S.S.R. and translated books were issued by the National Lending Library for Science and Technology of D.S.I.R. in October and November 1961 (see also *Talanta*, 1961, **8**, 690). To simplify and accelerate the compilation of the list, an English translation of each Russian title has now been omitted.

Literature available in the National Lending Library may be consulted in the reading room at Boston Spa, Yorkshire, between the hours of 9 a.m. and 5 p.m. on Mondays to Fridays excluding official holidays.

Publications listed by the Library may be borrowed by sending Science Museum Library loan requisition forms direct to Boston Spa. Organisations which at present do not borrow from the Science Museum Library, but wish to borrow literature from the National Lending Library, should write to the Keeper of the Science Museum Library, London, S.W.7, and ask to be considered for the Science Museum Library's list of approved borrowers. When approved in this way, loan requisition forms will be provided.

The following New British Standards are announced in *B.S.I. News: B. S.* 1728: *Methods for the analysis of aluminium and aluminium alloys: Part* 12: 1961: *Silicon.* This specifies reagents required, recommended methods of sampling, and analytical procedure for the determination of silicon in alloys having a silicon content of between 0.02 and 0.3%. (Price 3s.)

B.S. 3422: 1961: *Laboratory deflection pH meters.* This specifies essential performance requirements for laboratory deflection pH meters intended primarily for general laboratory use, and includes portable and battery operated instruments; it covers single pH scale and multi pH scale types. (Price 4s.)

Also announced are the following Revised British Standards:

B.S. 1121: *Methods for the analysis of iron and steel: Part* 20: 1961: *Tin in iron and steel.* This describes a method applicable to iron and steel containing up to 0.25% of tin. (Price 2s.6d.)

Part 37: 1961: *Nickel in iron and steel and permanent magnet alloys.* This describes two methods applicable to iron and steel and permanent magnet alloys. Method A covers the range of nickel contents in iron, steel, and permanent magnets of the aluminium-nickel-cobalt type, provided that the cobalt in the test solution does not exceed 0.15 g. Method B is intended for cobalt steels containing up to 0.25% of nickel, where the amount of cobalt in the test solution exceeds 0.15 g (Price 4s.) This method supersedes *B.S.* 1121: *Part* 2, which is now withdrawn.

B.S. 2058: 1961: *Lunge-Rey weighing pipette.* This specifies the material, construction, essential dimensions and inscriptions for the Lunge-Rey weighing pipette. (Price 4s.)

The following Amendment Slip is announced:

B.S. 1061: *Methods for the analysis and testing of coal and coke: Part* 5: 1957: *Gross calorific value of coal, and coke. Amendment No.* 2: *PD* 4309.

UNITED STATES OF AMERICA

Tuesday 9 *January–Thursday* 1 *February* 1962: **Fifteenth Annual Symposium on Modern Methods of Analytical Chemistry.** Louisiana State University, Baton Rouge, La.

Thursday–Friday 25–26 *January* 1962: **Analytical Division of Fourth Delaware Valley Regional Meeting.** Sheraton Hotel, Philadelphia. Two symposia are planned, one on the first day on Separation Techniques, and one on the second day on Laboratory Automation.

Monday 30 *April–Thursday* 3 *May* 1962: **Thirteenth Annual Mid-American Spectroscopy Symposium:** *Society for Applied Spectroscopy, Chicago Section in* co-operation with *Cleveland, Detroit, Indianapolis and St. Louis Sections.* Conrad Hilton Hotel, Chicago.

Original papers on the most recent advances in infrared, Raman, optical emission, X-ray, general absorption, nuclear magnetic resonance, electron spin resonance and atomic absorption will be presented. For the first time sessions on vacuum ultraviolet, gas chromatographic preparation of samples for spectroscopic analysis and a nuclear magnetic resonance workshop will be introduced. The popular introductory clinic in infrared spectroscopy will be continued, and problem clinics, seminars and an exhibit featuring the very latest instruments and equipment will be of special interest.

For further information write to Dr. JOHN R. FERRARO, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, U.S.A.

Monday–Friday 18–22 *June* 1962: **International Conference on Spectroscopy,** also designated **Xth Colloquium Spectroscopicum Internationale:** *Society for Applied Spectroscopy.* University of Maryland College Park, Md., near Washington, D.C.

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The purpose of the conference is to promote the exchange of knowledge on current research in important areas of spectroscopy, both basic and applied. The invited lecturers include:

H. KAISER (Dortmund, Germany)	*Critical Review of the Methods and Results of Time Resolved Spectroscopy.*
C. T. J. ALKEMADE (Utrecht, Netherlands)	*Excitation and Related Phenomena in Flames.*
A. WALSH (Melborne, Australia)	*Atomic Absorption Spectroscopy.*
J. L. GREENSTEIN (Pasadena, U.S.A.)	*The Role of Spectroscopy in Astrophysics.*
T. A. CHUBB (Washington, U.S.A.)	*Measurement of Ultraviolet and X-ray Radiation from above the Atmosphere.*
L. BELLAMY (Essex, England)	*Factors Influencing the Position of Group Frequencies in Infrared Spectra.*
H. H. GUNTHARD (Zurich, Switzerland)	(to be announced)
J. H. JAFFE (Rehovoth, Israel)	*Spectral Line Shape and Molecular Interaction*
R. N. JONES (Ottawa, Canada)	*Comparative Studies of Infrared and Raman Group Frequencies and their Applications.*
A. J. AHEARN (Murray Hill, U.S.A.)	*Vaccuum Spark Mass Spectrographic Analysis of Solids.*
J. BEYNON (Manchester, England)	*Correlation of Mass Spectra with Molecular Structure.*
C. HUTCHINSON (Chicago, U.S.A.)	*Electron Spin Resonance.*
R. RICHARDS (Oxford, England)	*Applications of Nuclear Magnetic Resonance.*
D. H. WHIFFEN (Teddington, England)	*Electron Spin Resonance and Free Radical Structure.*
B. VODAR (Bellevue)	*Extreme Ultraviolet Spectra.*
D. A. RAMSAY (Ottawa, Canada)	*Spectra of Gaseous Free Radicals.*
B. P. STOICHEFF (Ottawa, Canada)	*On the Application of Optical Masers to Spectroscopic Studies.*
J. PHILIBERT (St. Germain-en-Laye, France)	(to be announced)
V. B. COSSLETT (Cambridge, England)	(to be announced)

In addition to the invited speakers, papers may be submitted on the following spectroscopic subjects: atomic emission and absorption, astrophysical, infrared, Raman and microwave, mass spectrometry, nuclear magnetic resonance and electron spin paramagnetic resonance, ultraviolet and visible, X-ray emission and absorption, education.

Those desiring to present papers should submit titles and abstracts of 250–300 words, before 31 December, 1961, to BOURDON F. SCRIBER, General Chairman, International Conference on Spectroscopy, National Bureau of Standards, Washington 25, D.C., U.S.A.

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Talanta, 1961, Vol. 8, p. 916. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

A phosphorus pentoxide dessicant employing exfoliated vermiculite as carrier: G. FREDERICK SMITH and HARVEY DIEHL. (6 *October* 1961).

The determination of traces of ruthenium in samples of platinum by neutron-activation analysis: R. A. KILLICK and D. F. C. MORRIS. (6 *October* 1916).

The electrolytic oxidation of oxalate ion in the determination of calcium and magnesium: JOHN MARTIN and WALTER WAGNER. (7 *October* 1961).

Oxidimetric determination of organic compounds by means of strong oxidising agents—A review: G. DEN BOEF and H. L. POLAK. (13 *October* 1961).

Photometric titrations: J. P. PHILLIPS and ROSE C. COWLEY. (20 *October* 1961).

Determination of alkyl cellulose ethers by gas chromatography: JOHN G. COBLER, E. PAUL SAMSEL and GARTH H. BEAVER. (20 *October* 1961).

Selective chelatometry of Cu^{II} with ethylenediamine-N,N,N′,N′-tetra-n-propionic acid: I. P. SANDERSON and T. S. WEST. (26 *October* 1961).

Improved pyrogallol determination of niobium based upon extraction of a quaternary ammonium ion complex: JOSÉ A. CATOGGIO and L. B. ROGERS. (26 *October* 1961).

Improved determination of tantalum based upon the pyrogallol procedure: JOSÉ A. CATOGGIO and L. B. ROGERS. (26 *October* 1961).

Improved radiochemical determination of cobalt: S. FREDRIC MARSH and WILLIAM J. MAECK. (26 *October* 1961).

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